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SYNTHESIS OF MONOMERS FOR NEW CONJUGATED POLYMERS

A Thesis Presented

by

KEDAR GIRISH JADHAV

Submitted to the Graduate School of the

University of Massachusetts Amherst in partial fulfillment

of the requirements for the degree of

MASTER OF SCIENCE

February 2012

Organic Chemistry

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SYNTHESIS OF MONOMERS FOR NEW CONJUGATED POLYMERS

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DEDICATED

TO MY PARENTS

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ABSTRACT

SYNTHESIS OF MONOMERS FOR NEW CONJUGATED POLYMERS

FEBRUARY 2012

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Directed by: Professor D. Venkataraman

This Thesis addresses the problem of synthesis of different monomers for donor and acceptor polymers in photovoltaic applications. In general, functionalization of conjugated polymers and understanding of molecular packing of electron donors and electron acceptors are very important to produce efficient solar cells. As a result, it is important to design and synthesize novel monomers which will require making new π-conjugated donors and acceptors polymers and understand the influence of these new polymers in bulk heterojunction to design polymer solar cells. In this study, two different monomers were synthesized. The first monomer was designed and synthesized to investigate the effect of π-conjugated linker directly attached to the polymer backbone where the polymer backbone was based on thiophene unit and conjugated linker was 1,2,3-triazole. In a different study, a conjugated monomer based on benzthiadiazole was designed and synthesized in order to synthesize new acceptor homopolymers and alternating copolymers. Two different monomers with different alkyl side chains based on benzthiadiazole were synthesized and subject to Suzuki and Stille polymerization to get respective polymers.

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CHAPTER 1

1. INTRODUCTION

1.1 Overview and Principle of Organic Photovoltaics.

The exponential growth of energy needs in the world and the depletion of the fossil fuel reserves have brought a compelling situation to find an alternative energy source. Harvesting energy directly from sunlight using photovoltaic technology is an important way to address growing global energy needs using a renewable resource.[1] Although significant progress has been made for inorganic photovoltaic devices; they are still not cost effective, partially due to the requirement of highly pure silicon. In contrast to the inorganic photovoltaic devices, organic photovoltaic devices have advantages like light-weight, easy processability, flexibility in shape and low cost of production of the relevant dyes. Therefore, there is a widespread interest in developing devices based on organic materials for solar energy conversion.[2-8]

Polymeric solar cells (PSCs) have promising potential to offer clean and renewable energy due ease of fabricating them onto large areas of lightweight flexible substrates by solution processing at a low cost. But, the power conversion efficiency of these cells is very low as compared to inorganic devices due poor charge carrier generation and unbalanced charge transport.[9] So, it is necessary to understand basic principles of process of charge transfer in organic photovoltaic cell and develop new organic materials to achieve high efficiencies. The schematic representation of operating principle of organic photovoltaic cells is shown below.

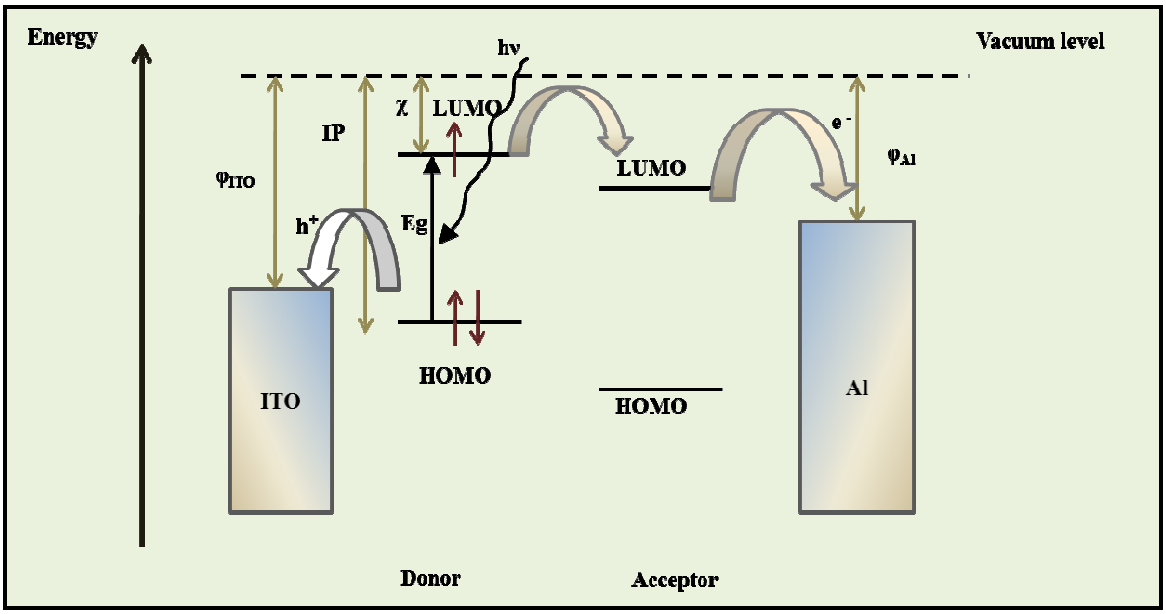


Figure 1.1 Schematic representation of operating principle of a photovoltaic cell.

Electrons are collected at the Al electrode and holes at the ITO electrode. Φ: workfunction, χ: electron affinity, IP: ionization potential, Eg: optical bandgap.

Generally a solar cell operates through four major steps.[10]The first step is absorption of incident photons, which depends on macroscopic surface property of the material used. After the absorption, it creates the electron hole pair called as excitons.[11]Third step is separation of the electron and hole which is determined by the charge distribution inside the cell. The final step is collection of the charge at respective electrodes which depends upon the Fermi level alignment of the metals with the energy levels of the material. Mainly the efficiency of a solar cell depends on the number of independent charge carriers produced through this procedure.

Based on above mentioned principle, many attempts have been made to design organic solar cells. Firstly, an organic photovoltaic cell with a single-component active layer sandwiched between two electrodes with different work functions was designed but

it led to very low power conversion efficiency.[9] Tang et al fabricated a bilayer heterojunction configuration containing a p-type layer as a hole transport and an n-type layer for electron transport to improve the photocurrent of the solar cell device.[12] In this case, as the generated excitons have very limited lifetime, it can only diffuse between 5-14 nm, [13, 14] reducing the probability of donor excitons to reach the acceptor. This leads to the loss of absorbed photons and quantum efficiency and therefore reducing performance of bilayer heterojunction devices. To overcome this difficulty, Yu et al.[15]developed the concept of a bulk heterojunction (BHJ). By blending donor and acceptor materials together, an interpenetrating network with a large donor-acceptor interfacial area can be achieved through controlling the phase separation between the two components in bulk. In a current scenario, most of the organic photovoltaic cells are designed on the concept of bulk heterojunction. In most common organic solar cell, a thiophene based conjugated polymer is used as the hole conductor, and a fullerene derivative ($PC_{61}BM$ or $PC_{71}BM$) is used as the electron conductor.

P3HT and $PC_{61}BM$ is the well-known system reported till date with an efficiency of 5%. [16]The efficiency can further be improved by tuning the properties of the thiophene based polymer backbone. The physical properties of polymers depend on the side chains or the solubilizing groups on the polymer and electronic properties depend upon energy levels of the polymer. These energy levels can be tuned either by changing the polymer backbone structure or by changing the nature of the side chains. In general, donor-acceptor type polymers exhibit low band gap and their HOMO and LUMO values can be tuned by altering the nature of the repeating unit. The electron donating side chains such as alkoxy, alkylthiols or alkylamines can push the HOMO up [17] and electron withdrawing

side chains such as acid or nitro group can pull the LUMO down.[18, 19] So, it is important to design new functionalized organic polymers which can be used to produce efficient solar cells.

Another approach to improve efficiency is to develop new -conjugated acceptor polymers that have absorption spectrum with better overlap with solar emission spectrum and have good electron transport. The most commonly used acceptor is Methanofullerene [6, 6]-phenyl C61-butyric acid methyl ester ($PC_{61}BM$). $PC_{61}BM$ is bulky in nature and segregates out while annealing P3HT-$PC_{61}BM$ blend due to mismatch in packing of these two materials.[20] Also, the energy levels of $PC_{61}BM$ cannot be tuned, restricting use of many donor organic materials in solar cells. One of the approach is to use tandem solar cells in which an additional hole conductor is used with in conjunction of donor and acceptor materials to broaden the absorption spectrum, thus in turn increasing efficiency of solar cell. It has been shown that, it can improve the efficiency of a solar cell but it is very difficult to obtain active layer morphology of both hole conductors with an acceptor molecule respectively. These are the reasons why, it is important to develop new -conjugated acceptor polymers which can have broad absorption spectra, good electron mobility and tunable energy levels.

1.2 Scope and Overview of thesis

Functionalization of conjugated polymers and understanding of molecular packing of electron donors and electron acceptors are very important to produce efficient solar cells. One of the main objectives of DV group at UMass Amherst is to synthesize novel π-conjugated donors and acceptor molecules and understanding the science behind assembling it to achieve proper molecular architecture and in turn increasing efficiency of

a solar cell. My Thesis mainly focuses on design and synthesis of novel monomers which will require making new π-conjugated donors and acceptors polymers and understanding the influence of these new polymers in bulk heterojunction to design polymer solar cells.

It has been known that functionalization of conjugated polymers with π-conjugated side chains is a very important tool to create next generation active materials for organic-based devices such as sensors, field effect transistors, and photovoltaic devices.[21] They offer high mobility and broad absorption bands in the UV-vis spectra. Functionalization of conjugated polymers can be achieved using 1, 3-dipolar cycloaddition. It is very important to design the monomers for the synthesis of these polymers as it may affect the method of polymerization and yields. Generally, functionalization of conjugated polymers with -conjugated side chains includes a non-conjugated spacer between the polymer backbone and side chain. This may influence the electronic properties of the polymer and in turn efficiency. So, it is necessary to investigate the effect of -conjugated linker directly attached to the polymer backbone. In addition to that, it is also essential to design the monomers to achieve the polymerization protocols. What will be effect on electronic properties on the polymer backbone with the direct attachment of -conjugated side chain as triazole? This is the research problem; I would like to answer in my thesis. This is important because we believe that triazole moiety in conjugation with a thiophene monomer can offer a convenient pathway to append -conjugated moieties to the conjugated polymer backbone and can alter the energy levels by either acting as donor-acceptor alternating polymers or by inductively changing the electron density.

In my second part of my thesis, I have focused on designing new monomers to develop novel -conjugated acceptor polymer based on benzthiadiazole. The idea behind

this research is to develop a new π-conjugated acceptor polymer which can absorb major portion of sunlight in solar spectrum. This is important because generally in most of organic photovoltaic cells, light absorption mainly done by donor part as its commonly used acceptor counterpart, $PC_{61}BM$, absorbs less than 350 nm. So, if one can develop an acceptor which can also absorb sunlight, it will increase photocurrent, in turn increasing efficiency of solar cell. Also, different donor materials can be used with newly synthesized π-conjugated acceptor polymer to design photovoltaic cells. It is well known from DV group research that the side chains can affect optical and electronic properties of polymers. So, we have incorporated two different side chains while designing the monomer to investigate the effect of side chains on optical and electrical properties. The long term goal is to develop a strategy to device a bulk heterojunction of newly synthesized π-conjugated acceptor polymers with different donor polymers to produce highly efficient solar cells.

The research part of my thesis is divided into two parts namely Chapter 2 and Chapter 3. Chapter 2 mainly discusses the issue of synthesis of new monomer where triazole is directly attached to thiophene as a conjugated side chain. This involves the problems faced during synthesis of monomers as well as polymers and different ways to overcome those synthetic difficulties. It also tries to answer the question of behavior of pendant triazole moiety as a side chain as compared with a triazole on the main chain and discusses about band gap of a polymer. Figure 2 shows the structures of synthesized monomers and polymers.

Figure 1.2 Structures of Monomer M1, M2 and Polyme

Chapter 3 explains synthesis of new acceptor monomers and polym solution to the problems encountered during the synthesis. It also helps the effect of side chains on optical and electronic properties of a polyme between repeating units plays an important role in optical properties of a 3 shows structures of newly synthesized acceptor monomers and polyme

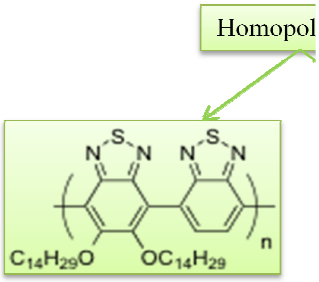


Figure 1.3 Structures of Monomer 1, Monomer 2, Homopolymers

Alternating copolymers (PBTDV)

The results from optical and electronics properties of acceptor polymers indicate that it has a lot of potential for organic PV devices.Chapter 2 and Chapter 3 mainly focused on design and synthesis of these new organic materials and characterization.

1.3 References

1. Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C., "Plastic solar cells," *Advanced Functional Materials* **2001**, 11-15.

2. Hoppe, H.; Sariciftci, N. S., "Organic solar cells: An Overview," *Journal of Materials Research* **2004**, *19*, 1924-1945.

3. Nogueira, A. F.; Longo, C.; De Paoli, M. A.," Polymers in dye sensitized solar cells: overview and perspectives," *Coordination Chemistry Reviews* **2004**, *248*, 1455-1468.

4. Spanggaard, H.; Krebs, F. C., "A brief history of the development of organic and polymeric photovoltaics," *Solar Energy Materials and Solar Cells* **2004**, *83*, 125-146.

5. Li, B.; Wang, L. D.; Kang, B. N.; Wang, P.; Qiu, Y., " Review of recent progress in solid state dye sensitized solar cells," *Solar Energy Materials and Solar Cells* **2006**, *90*, 549-573.

6. Riede, M.; Mueller, T.; Tress,W.; Schueppel, R.; Leo, K., " Small molecule solar cells - status and perspectives," *Nanotechnology* **2008**, *19*, 424001.

7. Yum, J. H.; Chen, P.; Gratzel, M.; Nazeeruddin, M. K., "Recent developments in solid-state dye sensitized solar cells," *ChemSusChem* **2008**, *1*, 699–707.

8. Bredas, J. L.; Norton, J. E.; Cornil, J.; Coropceanu, V., "Molecular understanding of organic solar cells: The challenges," *Accounts of Chemical Research* **2009**, *42*, 1691–1699.

9. Wohrle, D.; Meissner, D., "Organic solar cells," *Advanced Materials* **1991**, *3*, 129-138.

10. Nunzi, J. M., "Organic Photovoltaic Materials and Devices," *Comptes Rendus Physique* **2002**, *3*, 523-542.

11. Gregg, B. A., "Excitonic solar cells," *Journal of Physical Chemistry B* 2003,*107*, 4688-4698.

12. Tang, C. W., "Two-layer organic photovoltaic cell," *Applied Physics Letters* **1986**, *48*, 183.

13. Halls, J. J. M.; Pichler, K.; Friend, R. H.; Moratti, S. C.; Holmes, A. B., "Exciton diffusion and dissociation in a poly(*p*-phenylenevinylene)/C-60 heterojunction photovoltaic cell," *Applied Physics Letters* **1996**, *68*, 3120.

14. Haugeneder, A.; Neges, M.; Kallinger, C.; Spirkl, W.; Lemmer, U.; Feldmann, J.; Scherf, U.; Harth, E.; Gugel, A.; Mullen, K., " Exciton diffusion and dissociation in conjugated polymer/fullrene blends and heterostructures," *Physical Review B* **1999**, *59*, 15346-15351.

15. Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J., "Polymer photovoltaic cells: Enhanced efficiencies via a network of internal donor-acceptor heterojunctions," *Science* **1995**, *270*, 1789-1791.

16. Ma, W.; Yang, C.; Gong, X.; Heeger, A. J., "Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating control of morphology," *Advanced Functional Materials* **2005**, *15*, 1617-1622.

17. Ogawa, K.; Stafford, J. A.; Rothstein, S. D.; Tallman, D. E.; Rasmussen, S. C.," Nitrogen- functionalized polythiophenes: Potential routes to new low band gap materials," *Synthetic Metals* **2005,** *152*, 137-140.

18. Shi, C. J.; Yao, Y.; Yang, Y.; Pei, Q. B., "Regioregular copolymers of 3-alkoxythiophene and their photovoltaic application," *Journal of the American Chemical Society* **2006,** *128*, 8980-8986.

19. Murphy, A. R.; Liu, J. S.; Luscombe, C.; Kavulak, D.; Frechet, J. M. J.; Kline, R. J.; McGehee, M. D., "Synthesis, characterization, and field effect transistor performance of carboxylate functionalized polythiophenes with increased air stability," *Chemistry of Materials* **2005,** *17*, 4892-4899.

20. Yurt, S.; Venkatraman B.; Gavallaplli, N.; Venkataraman, D., "Role of molecular architecture in organic photovoltaic cells," *Journal of Physical Chemistry Letters* **2010**, *1*, 947-958.

21. Gavvalapalli, N.; Yurt, S.; Jadhav, K. G.; Venkataraman, D., "Impact of pendant 1, 2, 3-triazole on synthesis and properties of thiophene based polymers," *Macromolecules* **2010**, *43*, 8045-8050.

CHAPTER 2

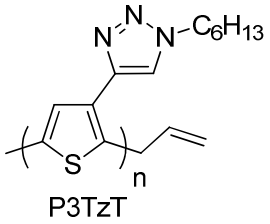
IMPACT OF PENDANT 1, 2, 3-TRIAZOLE ON SYNTHESIS AND PROPERTIES OF THIOPHENE MONOMERS AND POLYMERS.

2.1 Introduction

Organic polymer solar cells have several advantages as compared to inorganic materials such as low cost, flexibility and tunability of optical, electrical and chemical properties. These properties can be tuned by various structural modifications in the molecule. The physical properties such as solubility and processibility depend on the side chains or the solubilizing groups on the polymer, while the rest of the properties depend upon the FMO energy levels of the polymer. Functionalization of conjugated polymers with π-conjugated side chains is very essential in order to create new generation of active materials because of their high mobilities and presence of broad absorption bands in the UV-vis spectra.[1-7] The energy levels can be tuned either by changing the polymer backbone structure or by changing the nature of the side chains. In general, donor-acceptor type polymers exhibit low band gap and their HOMO and LUMO values can be tuned by altering the nature of the repeating unit.[8] The electron donating side chains such as alkoxy, alkylthiols or alkylamines can push the HOMO up,[9-11] and electron withdrawing side chains such as acid or nitro group can pull the LUMO down.[12-14] There have been several reports about donor-acceptor type polymers with thiophene as donor and five membered heterocycles such as thiazole, oxidiazole or 1,2,4-triazole (4RTaz/Th) as acceptors.[15-17] These polymers are observed to have a unique π-stacked structure assisted by charge transfer electronic structure. However, their optical and electrical

properties are not desirable. Also, it has not been studied the effect of attachment of heteroaromatic cycle (e.g. triazole) to the direct attachment to thiophene backbone on each repeating unit. These systems, depending on the nature of the conjugated heteroaromatic side chain can alter the energy levels by either acting as donor-acceptor alternating polymers or by inductively changing the electron density.

To answer the question of what is the effect of -conjugated linker directly attached to the polymer backbone, we have designed a protocol to synthesize a polymer wherein a triazole unit is directly attached to thiophene backbone. To functionalize the polymer we used 1,3-Dipolar cycloaddition[18] as it is widely used for the functionalization of polymers in general [19,20] and conjugated polymers in particular.[21,22] We chose to synthesize (poly(3-(1-hexyl-1H-1,2,3- triazole-4-yl)thiophene)), P3TzT, as this polymer would allow us to understand the impact of triazole on the electronic properties of the polythiophene backbone by comparing it with poly- (3-hexylthiophene) (P3HT), which is commonly used in organic electronic devices such as photovoltaic cells. The structure of the polymer has shown below in Figure 2.1.



P3TzT

Figure 2.1 Structure of Polymer P3TzT

2.2 Molecular Design and Synthesis of monomer

We synthesized the monomer for polymer (P3TzT) from readily available 3-bromothiophene which was converted to 3-iodothiophene (1) using the Finkelstein reaction.[23] The compound 1 was dibrominated using N-bromosuccinimide followed by the Sonogashira coupling with trimethylsilylacetylene and 1,3-dipolar cycloaddition with 1-azidohexane gave M1 in good yields.(Figure 2.2)

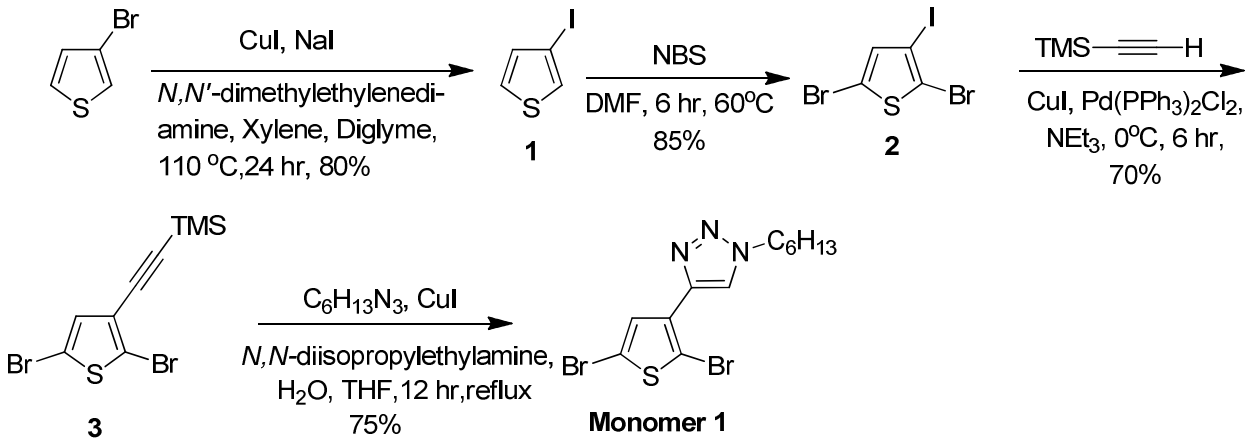


Figure 2.2 Synthesis Scheme for Monomer 1

We have used M1 to synthesize the polymer using standard Ni (0)-mediated Grignard metathesis polymerization (GRIM) condition.[24, 25] When the reaction mixture was poured into methanol; no precipitate was obtained, indicating the absence of polymeric products. We did not obtain a precipitate irrespective of whether the polymerization was done at room temperature or at elevated temperatures for 24 h. We hypothesized that the failure of the polymerization may be either due to the inability of M1 to undergo Grignard metathesis or the inability of the Grignard formed from M1to undergoNi(0)- mediated polymerization or both. So to overcome this problem, we have to

design an alternate synthesis route to synthesize the monomer which will yield expected polymer (P3TzT) and also it is necessary to understand why monomer M1 does not yield polymeric products.(Figure 2.3)

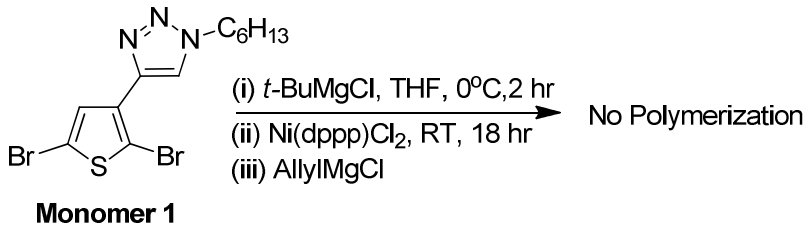


Figure 2.3 Synthesis route for polymerization from Monomer 1

2.3 Quenching Studies for Monomer M1

To understand why monomer M1 does not yield polymeric products using Grignard metathesis, we did quenching studies on monomer M1. Monomer M1 was reacted with t-BuMgCl for 2 h and the reaction mixture was quenched with H_2O (Figure 2.4). The organic components were extracted with diethyl ether, and the solvent was removed under reduced pressure. The ^1H NMR of residue showed presence of regioisomers.NMR results have shown that Grignard metathesis occurred with –Br group at second position which is *ortho* to triazole moiety. The reason of formation of Grignard at this position could be due to the coordination of triazole nitrogen and monomer acting chelating agent for Mg^{2+}.

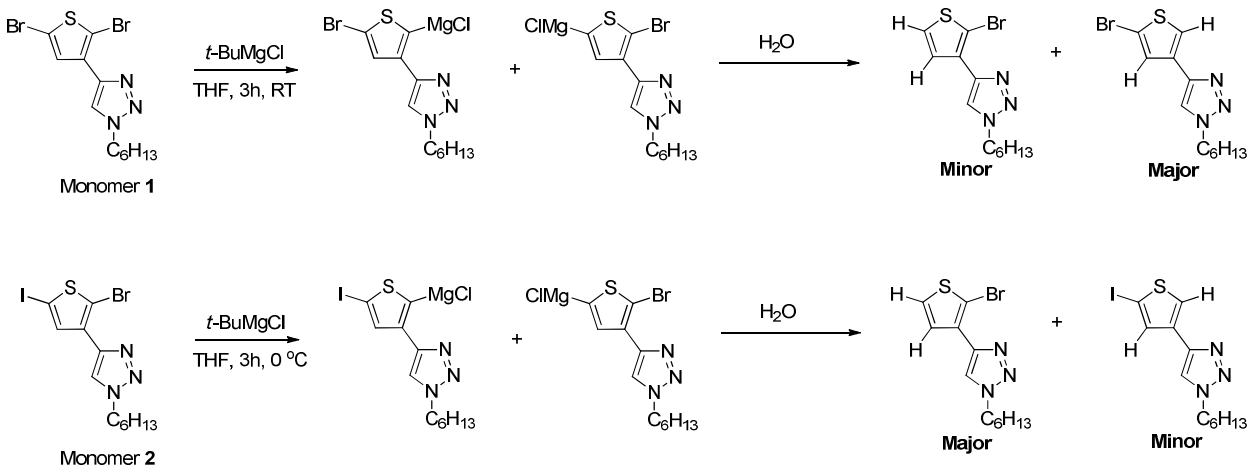


Figure 2.4 Quenching studies for Monomer 1

There have few reports in literature indicating that Grignard metathesis at second position can result in polymerization. Our result was consistent with previous studies [26, 27] with 5-bromo-2-iodo-3-hexylthiophene where it has been shown that there is no metal-halogen exchange at second position and it does not yield into polymerization. In this case, it has been argued that if the Grignard metathesis occurs at second position on the thiophene ring, then the Ni(0) does not insert in the carbon-bromine bond at the fifth position due to lack of stabilization from the alkyl chain at the third position. We hypothesize that in our case, since the hexyl group is away from the reaction side, the chelating ability of the triazole moiety may stabilize the Grignard or the nickel(II) complex that results from the Grignard and may prevent further reaction. As monomer M1 did not yield any polymer products, it was necessary to design a monomer which can direct Grignard metathesis at the fifth position of our thiophene monomer.

2.4 Alternate Synthesis Scheme

To overcome the problem of synthesis of polymer, it was necessary to design an alternative route to synthesize a monomer which can direct Grignard metathesis at fifth position of thiophene monomer. Since, it is known that Grignard metathesis occurs faster with a C-I than a C-Br bond, we expected that the Grignard reagent should preferentially react at the fifth position. So, we have designed a protocol to synthesize monomer M2 with iodine at the fifth position and bromine at the second position. The synthesis route for M2 has shown below in Figure 2.5.

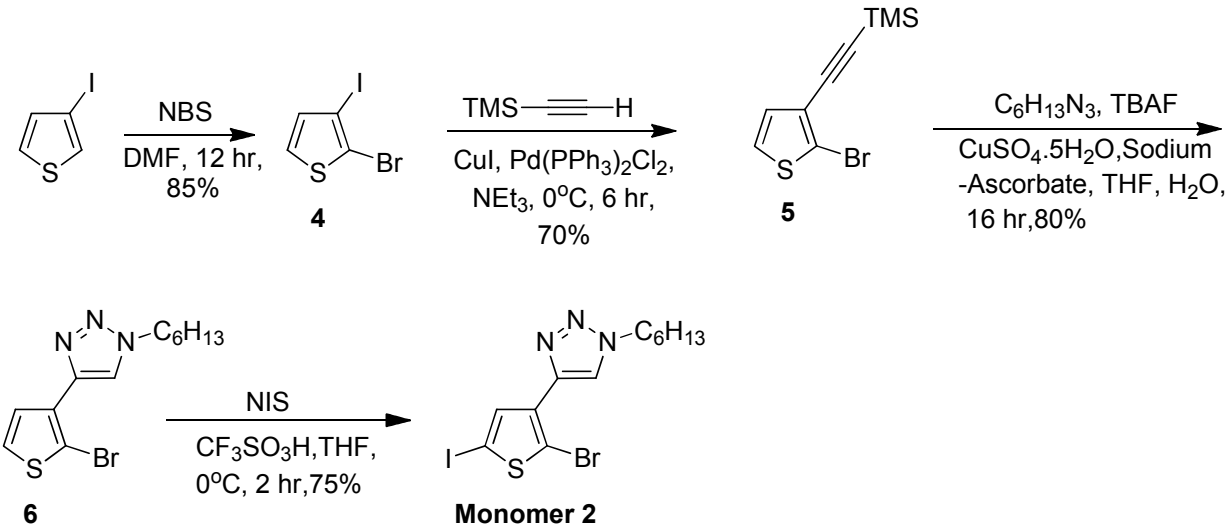


Figure 2.5 Synthesis scheme for Monomer 2

We synthesized the Monomer M2 for polymer (P3TzT) using almost same protocol with some modification in synthesis route. We started from readily available 3-bromothiophene which was converted to 3-iodothiophene (1) using the Finkelstein reaction. The compound was monobrominated using 1 equivalence of N-bromosuccinimide (NBS) followed by the Sonogashira coupling with

trimethylsilylacetylene and 1,3-dipolar cycloaddition with 1-azidohexane gave M2 in good yields. We screened a variety of iodination conditions and found that N-iodosuccinimide and trifluoromethanesulfonic acid (NIS/CF_3SO_3H) provided the iodinated compound in excellent yields.

M2 was reacted with t-BuMgCl, and the reaction mixture was quenched with water. NMR studies have shown that Grignard metathesis happening at the fifth position.[28] We were gratified to note that M2 was polymerized under GRIM conditions.(Figure 2.6) The polymer (P3TzT, Mn = 24.7 kDa, PDI = 1.48) was soluble in chloroform at room temperature and in DMF at elevated temperature.

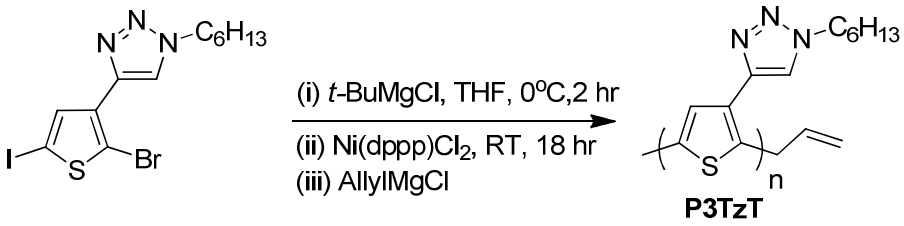


Figure 2.6 Polymer Synthesis from Monomer 2

2.5 UV-vis and Fluorescence studies of P3TzT

From the literature, it is evident that 1,2,3-triazole can act as an electron donor [29] or as an electron acceptor.[30] If triazole acts as electron donor, then it is expected that the HOMO levels of the polymer will be affected and if it acts as an acceptor the LUMO level of a conjugated polymer will get affected.[31-33] The resonance and inductive effects of triazole will also depend on the orientation of the triazole ring with respect to the backbone. Therefore, it is very importance to understand the impact of triazole on the

electronic structure of the conjugated polymer backbone and on the frontier energy levels.

The UV-vis absorption and fluorescence of the polymer was studied in solution as well as thin films. Solution state UV-vis and fluorescence spectra were recorded using a solution of polymer in chloroform and solid state measurements were done by casting a thin film of polymer from same solution and spectra were recorded before and after thermal annealing at 100 ^{o}C for 30 min. The absorption λmax in solution is 415 nm and in thin film is 506 nm with a red shift of 91 nm in thin films. In comparison, P3HT has a red shift of 115 nm in thin films.[28]

2.6 Fluorescence quenching with PCBM

To determine whether polymer P3TzT is a potential candidate for organic photovoltaic applications, fluorescence quenching studies were done with varying ratios of PCBM (0.1mg, 0.3mg, 0.6mg, 1.0mg of PCBM with 0.1mg of P3TzT respectively).[28] It was observed that the fluorescence intensity of P3TzT polymer decreased gradually with increase in weight ratio of PCBM. This has indicated that there is an electron transfer from P3TzT to PCBM resulting into fluorescence quenching. Thin film of 1:1 wt % P3TzT and PCBM was casted onto a glass plate did not show any fluorescence indicating complete fluorescence quenching of a polymer. Therefore, these studies prove that P3TzT is a potential candidate for organic photovoltaic applications.

2.7 Characterization

All the compounds were characterized by using ^{1}H NMR. NMRs for monomers are shown below. The NMR for Monomer 1 (Figure 2.7) indicates pure compound where in

2 protons in aromatic region corresponds to thiophene proton (7.64 ppm) and triazole proton (8.13 ppm). There is a triplet at 4.38-4.42 ppm corresponding to $–CH_2$ next to nitrogen of triazole unit. Other 11 protons of an alkyl chain falls in 0.87-1.98 ppm region.

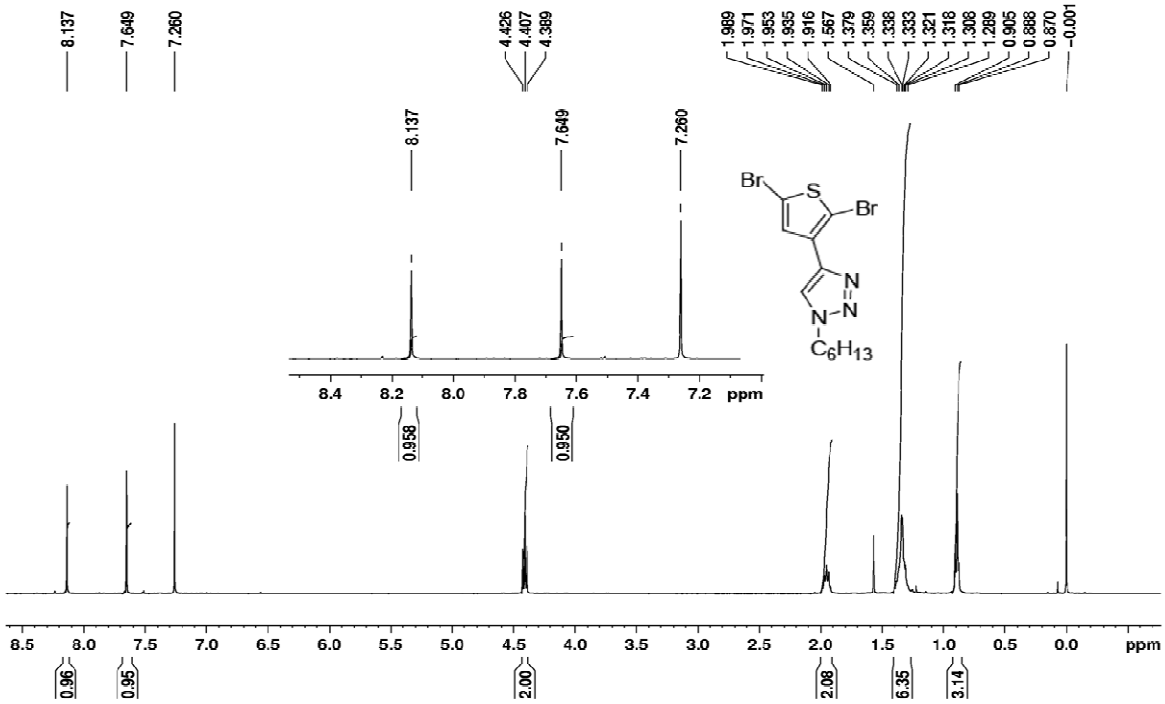


Figure 2.7 ^{1}H NMR of Monomer 1

In NMR spectra of Monomer 2 (Figure 2.8), there are 3 protons in aromatic region 1 from triazole (8.18 ppm) and other two were from thiophene proton (7.63 ppm and 7.31 ppm respectively). Triplet at 4.39 ppm corresponds to –CH2 next to nitrogen attached to triazole ring and all other protons of alkyl chain fall in region of 0.87-1.99 ppm. The NMR for Monomer 2 indicates pure compound where in 2 protons in aromatic region corresponds to thiophene proton (7.83 ppm) and triazole proton (8.14 ppm). There is a

triplet at 4.39-4.42 ppm corresponding to –CH2 next to nitrogen of triazole unit. Other 11 protons of an alkyl chain falls in 0.87-1.98 ppm region.

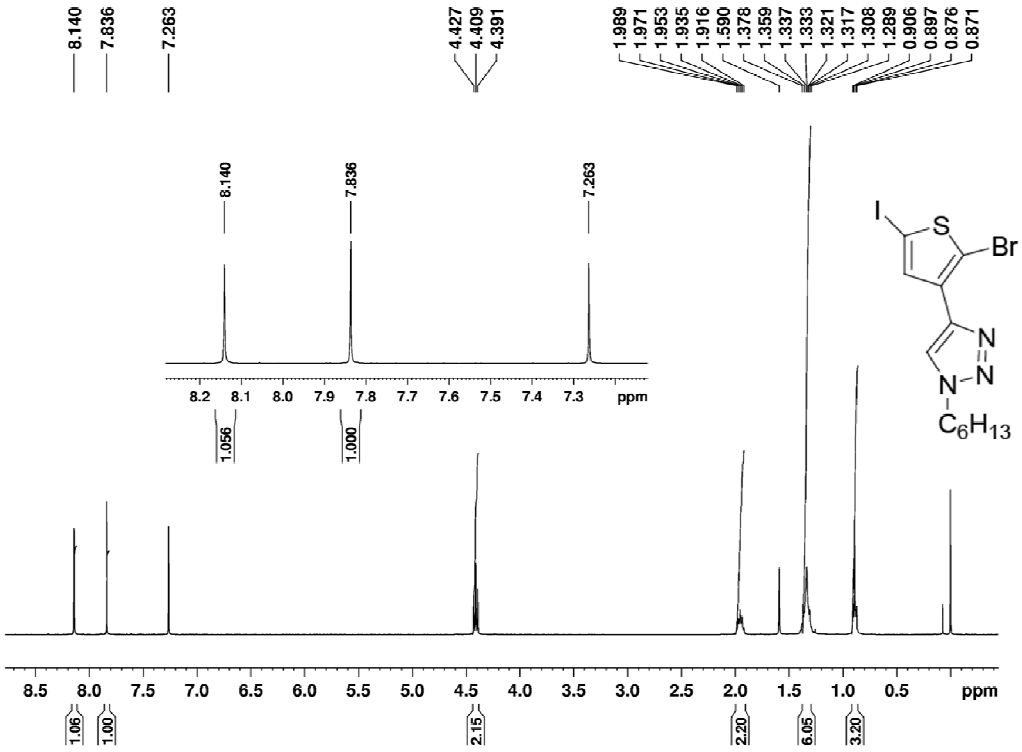


Figure 2.8 ^{1}H NMR of Monomer 2

2.8 Problems Associated with monomer synthesis

The monomer synthesis of Monomer 1 and Monomer 2 was done using the synthesis protocol shown in Fig. 1 and Fig.2. The Monomer 1 was synthesized from Compound 3 using 1,3 dipolar cycloaddition. In this case, the reagents used for click reaction were CuI

and DIPEA along with H_2O & THF as a solvent. The reaction worked very well producing high yields (75%) for corresponding click product i.e. Monomer 1 from compound 3. This reaction was carried out as shown below in Figure 2.9.

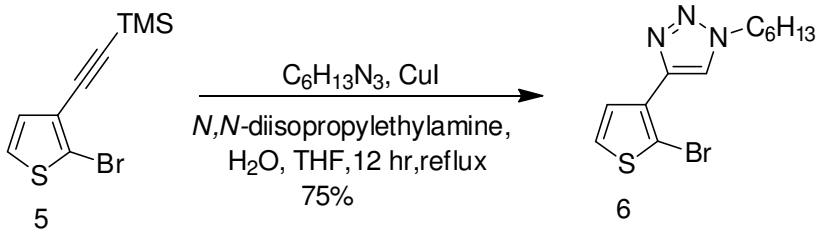


Figure 2.9 Synthesis of Compound 6 using CuI/DIPEA method

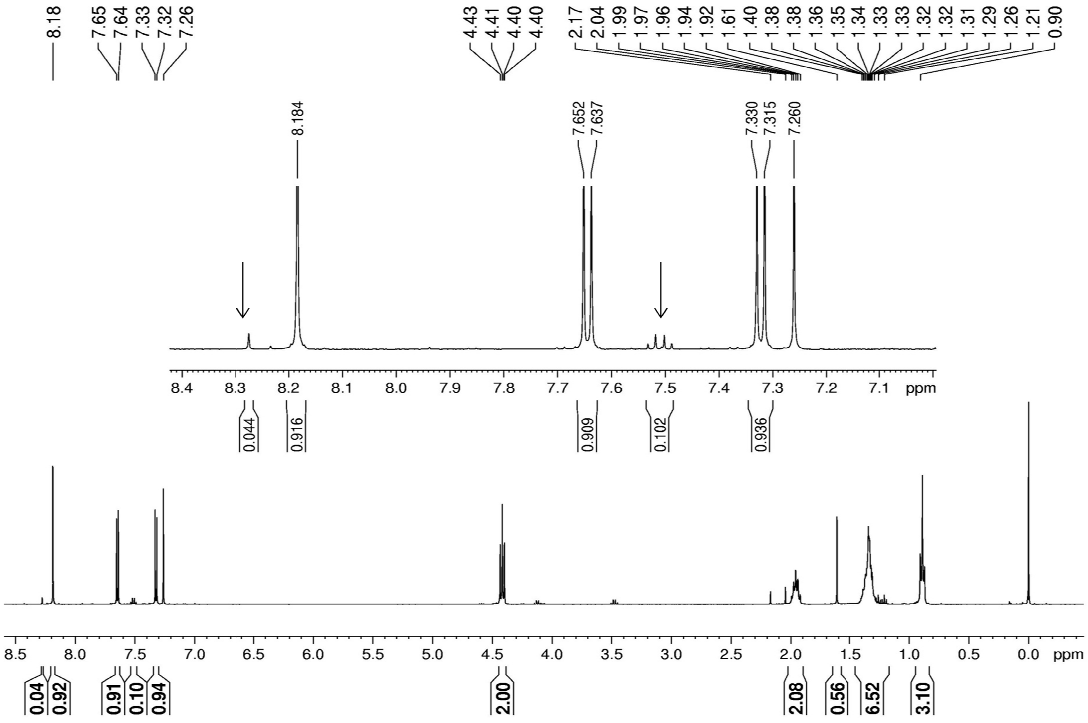


Figure 2.10 ^{1}H NMR of Click Reaction Product (Compound 6)

using CuI/DIPEA method

We have tried the similar protocol for our alternative synthesis scheme (Figure 2.9) to convert Compound 5 to Compound 6. But it has always shown some extra impurities peaks in ^{1}H NMR shown in Figure 2.10 below. We have tried to carry out the reaction in deoxygenated environment, but it has always shown the same impurity peaks in ^{1}H NMR. (Figure 2.10) Though the impurity were small in concentration, it was not preferable to carry out further steps with the same protocol.

We tried to find out the reason behind the formation of these impurities. Our reasonable guess was that there might be formation of diacetylene bond between two monomers or two monomers of compound 6 coming together to form a dimer. In the literature, it has been shown that these two structures can form during this type of reaction in small quantities.

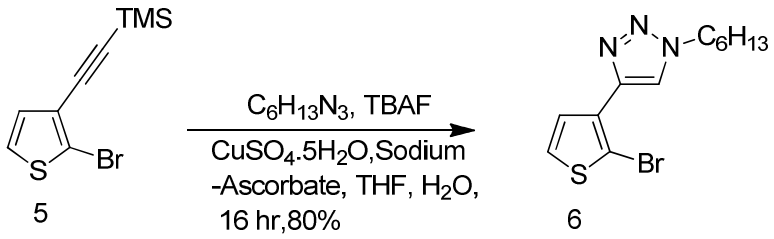


Figure 2.11 Synthesis of Compound 6 using $CuSO_4$/Sodium ascorbate method

To overcome this problem, we have decided to follow different protocol for click reaction. We have used $CuSO_4.5H_2O$, Sodium ascorbate along with TBAF for in-situ deprotection of TMS group. This protocol worked very well giving Compound 6 in very high yields (80%).(Figure 2.11) The NMR for this compound was shown below in Figure 2.12.

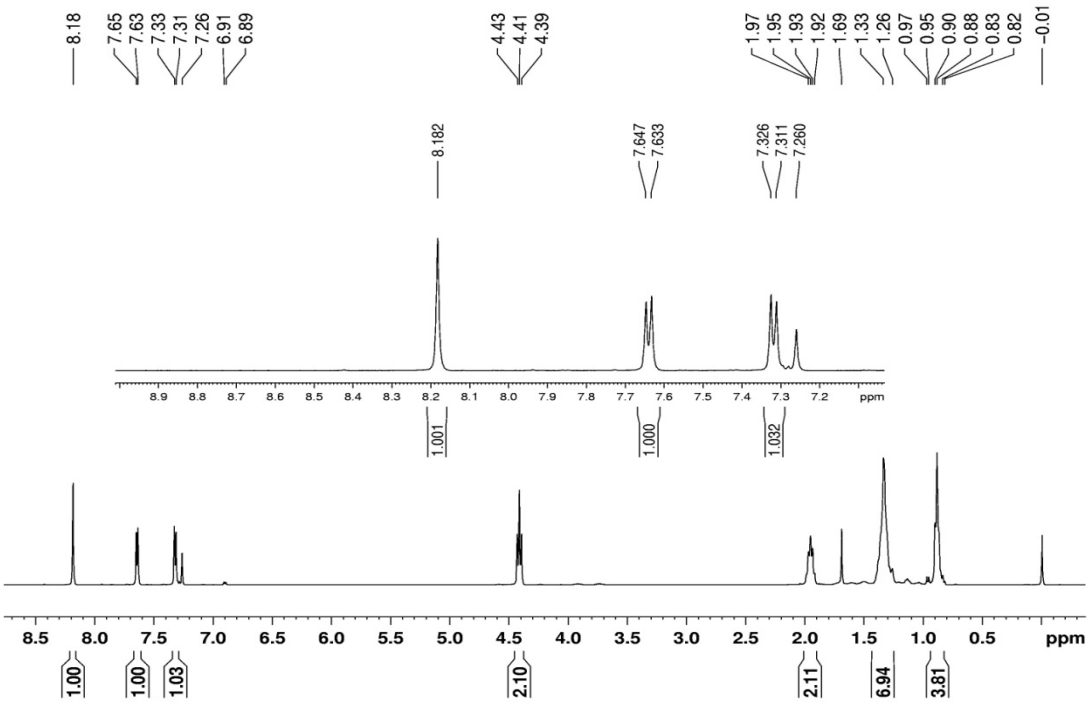


Figure 2.12 ^{1}H NMR of Click Reaction Product using

$CuSO_4$/Sodium ascorbate method

2.9 Conclusion and Future Work

The monomer synthesis of Monomer 1 and Monomer 2 for polymer P3TzT was not straightforward. The Monomer 1 did not go under polymerization due to formation of Grignard at 2nd position instead of 5th position on thiophene backbone of monomer 1. The reason of formation of Grignard at this position could be due to the coordination of triazole nitrogen and monomer acting chelating agent for Mg^{2+}. It has been identified that $CuSO_4$/Sodium ascorbate method gives pure products as compared to CuI/DIPEA method for Click reactions and also $CuSO_4$/Sodium ascorbate route eliminates possibility

of isomers during the reaction. It has been shown that P3TzT polymer can be synthesized using modified Monomer 2 in which 1,2,3- triazole moiety attached as a pendant group and polymerization can be done using Ni(0)-mediated Grignard metathesis polymerization. The triazole moiety also does not hinder the packing of the conjugated backbone. Fluorescence quenching of this polymer with PCBM indicates that it is a potential candidate for organic PV devices. The ongoing future work will be evaluating the hole mobilities and photovoltaic metrics of thiophene-based polymers with pendant triazole moiety with different kind of acceptors and new conjugated polymers.

2.10 Experimental Details

All chemicals were purchased from commercial sources (Acros, Aldrich, Alfa Aesar, TCI, and Strem) and used without further purification, unless otherwise noted. THF was distilled from sodium-benzophenone ketyl. NBS was recrystallized from water. Common solvents were purchased from EMD (through VWR). Routine monitoring of reactions was carried out on glass-supported EMD silica gel 60 F_{254} TLC plates. Flash chromatography was performed using silica gel from Sorbent Technologies (Standard Grade, 60 Å, 32-63 μm). All ^{1}H and ^{13}C $\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance400 spectrometer, unless otherwise noted. Chemical shifts and coupling constants (*J*) are reported in parts per million (δ) and Hertz, respectively. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. Chloroform-D ($CDCl_3$) contained 0.05% v/v tetramethylsilane (TMS) and Chloroform-D peak was set to 7.26 ppm on all proton spectra.

In Gel permeation chromatography (GPC) was done in the NSF-sponsored Materials Research Science and Engineering Center on Polymers (MRSEC) at the University of Massachusetts Amherst. GPC analyses were performed on a Polymer Laboratories GPC50 integrated system with DMF (1.0 mL/min, 120 °C) elution, 3 x Mixed C (300 x 7.5 mm) columns, and RI detection. Molecular weights were obtained based on PMMA standards, with toluene as the flow rate marker, and may be overestimated by a factor of 1.5-2.0.

UV-vis absorption spectra were measured with a Shimadzu UV 3600PC spectrometer Polymer-Based Materials Harvesting Solar Energy (Energy Frontier Research Center at the University of Massachusetts Amherst)EFRC laboratory. Stock solutions of polymers (*c*=1mg/10mL) were prepared in spectrophotometric grade chloroform (Fisher, Optima). UV–vis experiments for thin films were done by spin casting (1400 rpm) of 1 wt % solution of polymer in chloroform on a glass plate. Similarly, to the 1 wt % solution of polymer in chloroform PCBM (1:1 wt% with respect to polymer) was added and spin casted (600 rpm) onto a glass plate. These films were annealed at 100°C for 30 minutes, UV-Vis and Fluorescence spectra were recorded before and after annealing. Fluorescence spectra were measured on PTA flourimeter for thin films & on JASCO FP-6500 spectrofluorometer for solutions studies. Cyclic Voltammetry studies were done using BAS CV- 50 W instrument. Stock solutions of polymer (1wt% polymer in chloroform) were prepared & films are spin casted on the platinum working electrode CV was recorded with tetrabutylammonium hexfluorophosphate as a supporting electrolyte (0.1M) in acetonitrile. The redox potentials were determined versus an Ag/Ag^{+} reference electrode.The working and

auxiliary electrodes were cleaned after each run. HOMO and LUMO values were calculated using Fc/Fc^+ as a reference.

- **Monomer Syntheses**

3-iodothiophene (1). A Schlenk tube was charged with CuI (0.70 g, 3.68 mmol) and NaI (22.0 g, 147.2 mmol) under argon atmosphere. Xylene (57.6 mL) and diglyme (14.4 mL) were added followed by the addition of the ligand N, N-dimethylethylenediamine(0.79 g,7.36 mmol). Finally, 3-bromothiophene (12 g, 73.6 mmol) was added under nitrogen. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110° C for 22-24 h. The resulting suspension was allowed to reach room temperature. The solvents xylene & diglyme were removed under reduced pressure & the resulting mixture was extracted with hexanes (2x75 mL). The combined organics were washed with water (1x75mL), saturated NaCl solution (1x75 mL) and were dried over Na_2SO_4, concentrated, and the residue was purified by silica gel chromatography (hexanes) to provide (**1**) as a yellow liquid. (12.3g, 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 4.8, 3.0, 1H), 7.21-7.19 (m, 1H), 7.11-7.09 (dd, *J*= 4.8, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.74, 128.65, 127.34.

2,5-Dibromo-3-iodothiophene (2). In the absence of external light, N-Bromosuccinimide (NBS) (11.9 g, 66.6 mmol) was added to a round bottom flask equipped with stirrer and covered with an aluminum foil, in one portion, to a solution of (**1**) (7 g, 33.3 mmol) in DMF (200 mL).After stirring at room temperature for 1 h, the reaction mixture was heated and maintained to 60°C for 5 h and then quenched with water (200 mL). The reaction mixture was extracted with hexane (2x75mL) and layers

were separated. The organic layer was washed with water (2x75mL), saturated NaCl solution (1x75 mL) and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography (hexanes) afforded (**2)** (9.8 g, 80%) as pale yellow liquid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.08, 116.31, 113.46, 85.21.

(2, 5-Dibromo-thiopen-3-ylethnyl)-trimethyl-silane (3). A Schlenk tube was charged with CuI (0.052 g, 0.27 mmol) and Pd $(PPh_3)_2Cl_2$ (0.39 g, 0.55 mmol) under argon atmosphere. Triethylamine (TEA) (60 mL) was added to it and degassed. The reaction mixture brought to 0° C, followed by the addition of (**2)** (4.0 g, 13.9 mmol) and trimethylsilylacetylene (1.5 g, 15.2 mmol) and stirred for further 6 h maintaining the temperature at 0°C. The solvent TEA was removed under reduced pressure and the resulting mixture was extracted with hexanes (2x50 mL). The organic layer was washed with water (1x75 mL), saturated NaCl solution (1x50 mL) and was dried over Na_2SO_4, concentrated, and the residue was purified by silica gel chromatography (hexanes) to provide (**3)** (2.57 g, 70%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 1H), 0.25 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.15, 125.25, 116.84, 110.82, 99.69 ,97.00

1-Azido hexane

In a round bottom flask charged with stirrer, DMSO (60 mL), 1-bromohexane (5 g, 3.62 mmol) and sodium azide (3.52g, 5.43 mmol) were added and stirred it overnight. Water was added to quench the reaction and extracted with ethyl acetate (2x50mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate (1x25mL). The combined organics were washed with water (2x50mL), saturated NaCl solution

(1x50 mL) and dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the colorless oily liquid as product in (3.15 g, 82%) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (t, *J* = 7.0, 2H), 1.60-1.53 (m, 2H), 1.36-1.29 (m, 6H),0.89 (t, *J* = 7.0, 2H)

4-(2, 5-Dibromo-thiophen-3-yl)-1-hexyl-1*H*-[1, 2, 3]triazole (M1)

To an oven dried round bottom flask, was added CuI (0.472 g, 2.48 mmol) and THF (50 mL). To this stirred solution, *N*,*N*-Diisopropylethylamine (3.845 g, 29.81 mmol) and water (10 mL) was added followed by the addition of monomer (2,5-Dibromo-thiopen-3-ylethnyl)-trimethyl-silane **(3)** (1.68 g, 4.96 mmol) and 1-azido hexane (0.947 g, 7.45 mmol). The reaction was stirred for 15 h under reflux conditions. The reaction was quenched with water and extracted with ethyl acetate (2x50mL). The organics were washed with water (2x50 mL), saturated NaCl solution (1x50 mL)dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography (20:80 EtOAc: hexanes) afforded (**M1)** as white solid in (1.37 g, 70%) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.64 (s, 1H), 4.42 (t, *J* = 7.0, 2H), 1.98-1.91 (m, 2H), 1.37-1.29 (m, 6H), 0.90 (t, *J*= 7.0, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.03, 132.61, 131.35, 120.65, 112.52, 107.02, 50.58, 31.14, 29.72, 26.15, 22.43, 13.96. MS (FAB+) *m/z* 393.9 $[M+H]^+$

2-Bromo-3-iodo-thiophene (4)

In the absence of external light, N- Bromosuccinimide (NBS) (7.8 g, 49.22 mmol) was added to a round bottom flask which was charged with stirrer and covered with an aluminum foil, in one portion, to a solution of (**1)** (8.1 g, 44.74 mmol) in DMF (200

mL).After stirring at room temperature for 12 h, the reaction was quenched with water (200 mL) and extracted with hexanes (2x75 mL). The combined organics were washed with water (2x75 mL), saturated NaCl solution (1x75 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography (hexanes) afforded (**4)** (8.35 g, 75%) as pale yellow liquid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.24 (d, *J*= 5.6, 1H), 6.95-6.96 (d, *J*= 5.6, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.08, 116.31, 113.46, 85.21.

(2-Bromo-thiophen-3-ylethynyl)-trimethyl-silane (5)

A Schlenk tube was charged with CuI (0.105 g, 0.55 mmol) and $Pd(PPh_3)_2Cl_2$ (0.77 g,1.1 mmol) under argon. Triethylamine (TEA) (110 mL) was added to it and degassed. The reaction mixture brought to 0^{o}C, followed by the addition of (**4)** (8.0 g, 27.68 mmol) and trimethylsilylacetylene (2.99 g, 30.45 mmol) and stirred for further 6 h maintaining the temperature at 0° C. The reaction mixture was brought to room temperature and further stirred for 12 h. The solvent TEA was removed under reduced pressure and the resulting mixture was extracted with hexanes (2x50 mL). The combined organics were washed with water (1x75 mL), saturated NaCl solution (1x50 mL) and were dried over Na_2SO_4, concentrated, and the residue was purified by silica gel chromatography (hexanes) to provide (**5)** (5.02 g, 70%) as a yellow liquid. **.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.16 (d, *J*=6.0, 1H), 6.94-6.96 (d, *J*= 5.6, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.93, 125.61, 124.56, 117.83, 98.83, 98.07.

4-(2-Bromo-thiophen-3-yl)-1-hexyl-1*H*-[1,2,3] triazole (6)

To an oven dried round bottom flask, was added $CuSO_4.5H_2O$(462.15 mg, 1.85 mmol) and sodium ascorbate (1.83 g, 9.25 mmol) followed by the addition of tetra-*n*-butyl ammonium fluoride (TBAF) (37 mL) and tetrahydrofuran (THF) (150 mL). To this stirred solution, water (50 mL) was added followed by the addition of 1-azido hexane (4.7 g, 37.03 mmol) and (2,5-Dibromo-thiopen-3-ylethnyl)-trimethyl-silane **(5)** (4.8 g,18.51 mmol). The reaction was stirred for 16 h. The reaction was quenched with water and extracted with ethyl acetate (2x50 mL). The combined organics were washed with water (2x50 mL), saturated NaCl solution (1x50 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography (20:80 EtOAc: hexanes) afforded (**6)** as colorless oil (4.07 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.63-7.65 (d, *J*=5.6, 1H), 7.31-7.32(d, *J*=5.6, 1H),4.39-4.42 (t, *J*= 7.0, 2H), 1.98-1.91 (m, 2H), 1.37-1.29 (m, 6H), 0.87-0.90(t, *J*= 7.0, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 131.8, 127. 92, 126.36, 120. 60, 108.2, 50.50, 31.15, 30.32, 26.15, 22.44, 13.97.

4-(2-Bromo-5-iodo-thiophen-3-yl)-1-hexyl-1*H*-[1, 2, 3]triazole (M2)

Compound (**6)** (1.6 g, 5.091 mmol) was dissolved in dichloromethane in a Schlenk flask. To this solution, trifluoromethanesulfonic acid (3.82 g, 25.45 mmol) was added and the solution is cooled to 0°C using an ice bath. N-iodo succinamide (1.15 g, 5.091 mmol) was added in small portions and the reaction mixture and stirred for 2 h at room temperature. The reaction mixture was quenched with ice-water and extracted with CH_2Cl_2 (3x25 mL)**.** The combined organic extracts were washed with aqueous 10 %

sodium bisulfate solution and water (2x25 mL), saturated NaCl solution (1x25 mL) and dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified by silica gel chromatography (15:85 EtOAc: hexanes) to provide (**M2)** as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.85 (s, 1H), 4.42 (t, *J* =7.0, 2H), 1.98-1.91 (m, 2H), 1.37-1.29 (m,6H),0.90(t,*J*=7.0,3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 140.84, 137.63, 133.85, 120.61, 110.84, 72.68, 50.70, 31.27, 30.42, 26.28, 22.56, 14.09.

4-([2,2':5',2''-terthiophen]-3'-yl)-1-hexyl-1*H*-1,2,3-triazole (7)

To an oven dried Schlenk, compound (**6)** (100 mg, 0.254 mmol) was added followed by the addition of Pd $(PPh_3)_4$ (29.35 mg, 0.025 mmol) in glove box. Dry THF (7.5 mL, 0.034 M) was deoxygenated for 2 h and added to the Schlenk. Aqueous K_2CO_3 (1 mL, 0.25 M) was added and the reaction mixture was stirred for 15 minutes. To this, 2-thiophene boric acid (127.6 mg, 0.997 mmol) was added and further stirred for 36 h at 60 °C. After stirring for 36 h, water was added to the mixture and then extracted with ethyl acetate (2x25 mL). The combined organics were washed with water (2x25mL), saturated NaCl solution (1x25 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography (30:70 EtOAc: hexanes) afforded the product (**7)** (70%). ^{1}H NMR (400MHz, CD_3COCD_3) δ 7.83 (s, 1H), 7.59 (s, 1H), 7.54- 7.55 (dd, *J*= 5.2, 1H), 7.47- 7.49 (dd, *J*= 5.2, 1H), 7.36 (dd, *J*= 3.6, 1H), 7.35 (dd, *J*=3.6, 1H), 7.10 (dd, *J*= 5.2, 2H), 4.39 (t, *J*= 7.0, 2H), 1.85- 1.91(m, 2H), 1.28- 1.30 (m, 6H), 0.88 (t, *J*= 7.0, 3H). ^{13}C NMR (100 MHz, CD_3COCD_3) δ 142.46, 137.21, 137.08, 135.22, 131.28, 130.84, 129.19, 129.09, 128.69, 128.15, 126.41, 125.34, 123.0, 50.71, 31.96, 31.08, 23.23, 14.33

- **Polymer Synthesis**

M2 (150 mg, 0.340 mmol) was dissolved in dry THF into the Schlenk flask covered with aluminum foil under argon atmosphere. The Schlenk was cooled to 0° C using an ice bath. The reagent *t*-butylmagnesium chloride (0.22 mL, 0.374 mmol) (1.7 M in THF) was added to the solution with a syringe and the mixture was allowed to stir for 2 h. Ni(dppp)Cl_2 (1.37 mg, 0.0025 mmol) was added under argon atmosphere. The reaction mixture was taken out from the ice bath and allowed to run for 18 h at room temprature and then quenched using allyl magnesium chloride (0.02 mL, 0.034 mmol). The reaction mixture was precipitated in ice-cold methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, $CHCl_3$. The $CHCl_3$ fraction, after concentration under reduced pressure, afforded 52 mg of the polymer. The material isolated from the hexanes fraction was analyzed by GPC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.64 (s, 1H), 4.36-4.40 (t, *J* =7.0, 2H), 1.87-1.95 (m, 2H), 1.22-1.34 (m, 6H), 0.81-0.83(t, *J*=7.0, 3H). M_n= 24.7k, PDI= 1.48

- **Attempted Synthesis of Monomers**

M1 (300 mg, 0.763 mmol) was dissolved in dry THF into the Schlenk flask under argon atmosphere. The reagent *t*-butylmagnesium chloride (0.49 mL, 0.839 mmol) (1.7 M in THF) was added to the solution with a syringe and the mixture was allowed to stir for 3 h. After 3 h, Ni(dppp)Cl_2 (4.18 mg, 0.0076 mmol) was added under argon atmosphere. The reaction mixture was allowed to run for 24 h at room temprature and then quenched using allylmagnesium chloride (0.044 mL, 0.076 mmol). The reaction mixture was added to ice-cold methanol, but no precipitate was observed.

M1 (300 mg, 0.763 mmol) was dissolved in dry THF into the Schlenk flask under argon atmosphere. The reagent *t*-butylmagnesium chloride (0.49 mL, 0.839 mmol) (1.7 M in THF) was added to the solution with a syringe and the mixture was allowed to stir for 3 h. After 3 h, Ni(dppp)Cl_2 (4.18 mg, 0.0076 mmol) was added under argon atmosphere. The reaction mixture was allowed to run for 24 h at 60 °C. After 24 h, the reaction mixture was brought to room temperature and then quenched using allylmagnesium chloride (0.044 mL, 0.076 mmol). The reaction mixture was added to ice-cold methanol, but no precipitate was observed

2.11 References

1. Park, J. W.; Lee, D. H.; Chung, D. S.; Kang, D. M.; Kim, Y. H.; Park, C. E.; Kwon, S. K., "Conformationally Twisted Semiconducting Polythiophene Derivatives with Alkylthiophene Side Chain: High Solubility and Air Stability", *Macromolecules* **2010**, *43*, 2118–2123.

2. Yu, C. Y.; Ko, B. T.; Ting, C.; Chen, C. P., "Two-dimensional regioregular polythiophenes with conjugated side chains for use in organic solar cells", *Solar Energy Materials and Solar Cells* **2009**, *93*, 613–620.

3. Zou, Y. P.; Sang, G. Y.; Wu, W.P.; Liu, Y. Q.; Li, Y. F., "A polythiophene derivative with octyloxyl triphenylamine-vinylene conjugated side chain: Synthesis and its applications in field-effect transistor and polymer solar cell", *Synthetic Metals* **2009**, *159*, 182–187.

4. He, Y. J.; Wu, W. P.; Liu, Y. Q.; Li, Y. F., "High performance polymer field-effect transistors based on polythiophene derivative with conjugated side chain", *Journal of Polymer Science Part A-1: Polymer Chemistry* **2009**, *47*, 5304–5312.

5. Huang, F.; Chen, K. S.; Yip, H. L.; Hau, S. K.; Acton, O.; Zhang, Y.;Luo, J.D.; Jen, A. K. Y., "Development of New Conjugated Polymers with Donor−π-Bridge−Acceptor Side Chains for High Performance Solar Cells", *Journal of American Chemical Society* **2009**, *131*, 13886–13887.

6. Huo, L. J.; Tan, Z. A.; Wang, X.; Zhou, Y.; Han, M. F.; Li, Y. F., "Novel two-dimensional donor–acceptor conjugated polymers containing quinoxaline units:

Synthesis, characterization, and photovoltaic properties", *Journal of Polymer Science Part A-1: Polymer Chemistry* **2008**, *46*, 4038–4049.

7. Shen, P.; Sang, G. Y.; Lu, J. J.; Zhao, B.; Wan, M. X.; Zou, Y. P.; Li, Y. F.; Tan, S. T., "Effect of 3D π–π Stacking on Photovoltaic and Electroluminescent Properties in Triphenylamine-containing Poly(*p*-phenylenevinylene) Derivatives", *Macromolecules* **2008**, *41*, 5716–5722.

8. Price, S. C.; Stuart, A. C.; You, W., "Polycyclic Aromatics with Flanking Thiophenes: Tuning Energy Level and Band Gap of Conjugated Polymers for Bulk Heterojunction Photovoltaics", *Macromolecules* **2010,** *43*, 797-804.

9. Huo, L. J.; Yi, Z.; Li, Y. F., "Alkylthio-Substituted Polythiophene: Absorption and Photovoltaic Properties", *Macromolecular Rapid Communications* **2009,** *30*, 925-931.

10. Ogawa, K.; Stafford, J. A.; Rothstein, S. D.; Tallman, D. E.; Rasmussen, S. C., "Nitrogen-functionalized polythiophenes: Potential routes to new low band gap materials", *Synthetic Metals* **2005,** *152*, 137-140.

11. Shi, C. J.; Yao, Y.; Yang, Y.; Pei, Q. B., "Regioregular Copolymers of 3-Alkoxythiophene and Their Photovoltaic Application", *Journal of American Chemical Society* **2006,** *128*, 8980-8986.

12. Pomerantz, M.; Cheng, Y.; Kasim, R. K.; Elsenbaumer, R. L., "Poly(alkyl thiophene-3-carboxylates).Synthesis, properties and electroluminescence studies of polythiophenes containing a carbonyl group directly attached to the ring", Journal *of Materials Chemistry* **1999,** *9*, 2155-2163.

13. Devasagayaraj, A.; Tour, J. M., "Synthesis of a Conjugated Donor/Acceptor/Passivator (DAP) Polymer", *Macromolecules* **1999,** *32*, 6425-6430.

14. Murphy, A. R.; Liu, J. S.; Luscombe, C.; Kavulak, D.; Frechet, J. M. J.; Kline, R. J.; McGehee, M. D., "Synthesis, Characterization, and Field-Effect Transistor Performance of Carboxylate-Functionalized Polythiophenes with Increased Air Stability", *Chemistry of Materials* **2005,** *17*, 4892-4899.

15. Yasuda, T.; Imase, T.; Sasaki, S.; Yamamoto, T., "Synthesis, Solid Structure, and Optical Properties of New Thiophene-Based Alternating π-Conjugated Copolymers Containing 4-Alkyl-1,2,4-triazole or 1,3,4-Thiadiazole Unit as the Partner", *Macromolecules* **2005,** *38*, 1500-1503.

16. Ng, S. C.; Ding, M.; Chan, H. S. O.; Yu, W. L., "The Synthesis and Characterization of Fluorescent Poly(heteroaromatic oxadiazole)s", *Macromolecular Chemistry and Physics* **2001,** *202*, 8-13.

17. Yasuda, T.; Namekawa, K.; Iijima, T.; Yamamoto, T., "New luminescent 1,2,4-triazole/thiophene alternating copolymers: Synthesis, characterization, and optical properties", *Polymer* **2007,** *48*, 4375-4384.

18. Kolb, H. C.; Finn, M. G.; Sharpless, K. B., "Click Chemistry: Diverse Chemical Function from a Few Good Reactions", *Angewandte Chemie International Edition* **2001**, *40*, 2004–2021.

19. Fournier, D.; Du Prez, F., ""Click" Chemistry as a Promising Tool for Side-Chain Functionalization of polyurethanes", *Macromolecules* **2008**, *41*, 4622–4630.

20. Binder, W. H.; Sachsenhofer, R., "'Click' Chemistry in Polymer and Materials Science", *Macromolecular Rapid Communications* **2007**, *28*, 15–54.

21. Benanti, T. L.; Kalaydjian, A.; Venkataraman,D., "Protocols for Efficient Postpolymerization Functionalization of Regioregular Polythiophenes", *Macromolecules* **2008**, *41*, 8312–8315.

22. Zeng, Q.; Li, Z.; Li, Z.; Ye, C.; Qin, J.; Tang, B. Z., "Convenient Attachment of Highly Polar Azo Chromophore Moieties to Disubstituted Polyacetylene through Polymer Reactions by Using "Click" Chemistry", *Macromolecules* **2007**, *40*, 5634–5637.

23. Klapars, A.; Buchwald, S. L., "Copper-Catalyzed Halogen Exchange in Aryl Halides: An Aromatic Finkelstein Reaction", *Journal of American Chemical Society* **2002**, *124*, 14844–14845.

24. Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D., "A Simple Method to Prepare Head-to-Tail Coupled, Regioregular Poly(3-alkylthiophenes) Using Grignard Metathesis", *Advanced Materials* **1999**, *11*, 250–253.

25. Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D., "Experimental Evidence for the Quasi-"Living" Nature of the Grignard Metathesis Method for the Synthesis of Regioregular Poly(3-alkylthiophenes)", *Macromolecules* **2005**, *38*, 8649–8656.

26. Boyd, S. D.; Jen, A. K. Y.; Luscombe, C.K., "Steric Stabilization Effects in Nickel-Catalyzed Regioregular Poly(3-hexylthiophene) Synthesis", *Macromolecules* **2009**, *42*, 9387–9389.

27. Loewe, R. S.; Ewbank, P. C.; Liu, J. S.; Zhai, L.; McCullough, R. D., "Regioregular, Head-to-Tail Coupled Poly(3-alkylthiophenes) Made Easy by the GRIM Method: Investigation of the Reaction and the Origin of Regioselectivity", *Macromolecules* **2001**, *34*, 4324–4333.

28. Nagarjuna, G.; Yurt, S.; Jadhav, K.G.; Venkataraman, D., "Impact of Pendant 1,2,3-Triazole on the Synthesis and Properties of Thiophene-Based Polymers", *Macromolecules* **2010**, *43*, 8045– 8050.

29. Zhou, Z.; Fahrni, C. J., "A Fluorogenic Probe for the Copper(I)-Catalyzed Azide–Alkyne Ligation Reaction: Modulation of the Fluorescence Emission via $^3(n,\pi^*)-(\pi,\pi^*)$ Inversion", *Journal of American Chemical Society* **2004**, *126*, 8862–8863.

30. Parent, M.; Mongin, O.; Kamada, K.; Katan, C.; Blanchard- Desce, M., "New chromophores from click chemistry for two-photon absorption and tuneable photoluminescence", *Chemical Communications* **2005**, 2029–2031.

31. Bundgaard, E.; Krebs, F. C., "Low band gap polymers for organic photovoltaics", *Solar Energy Materials and Solar Cells* **2007**, *91*, 954–985.

32. Ajayaghosh, A., "Donor–acceptor type low band gap polymers: polysquaraines and related systems", *Chemical Society Reviews* **2003**, *32*, 181–191.

33. Zeng, G.; Chua, S. J.; Huang, W., "Influence of donor and acceptor substituents on the electronic characteristics of poly(fluorene–phenylene)", *Thin Solid Films* **2002**, *417*, 194–197.

34. Bredas, J. L.; Heeger, A. J., “Influence of donor and acceptor substituents on the electronic characteristics of poly(paraphenylene vinylene) and poly(paraphenylene)”, *Chemical Physics Letters* **1994**, *217*, 507–512.

CHAPTER 3

SYNTHESIS OF NEW CONJUGATED ACCEPTOR MONOMERS AND POLYMERS BASED ON BENZTHIADIAZOLE

3.1 Introduction

Organic solar cells with bulk heterojunction offer a promising approach to solar energy problem at lower cost compared to inorganic solar cells.[1-4] The most efficient bulk heterojunction organic solar cells use a conjugated polymer as the donor which is p-type material[5-7] and fullrene derivative of C60 or C70 as an acceptor n-type material.[8,9] Most commonly used fullrene derivatives are [60]PCBM and [70]PCBM. These derivatives have good electron mobility[10] due to their semicrystalline nature[11] and offer solubility in a range of organic solvents for easy processing. But the main disadvantage is that their absorption of solar light is not very good, especially for C60 derivatives. So, one of the challenges in the field of organic photovoltaics is developing alternatives to the family of fullerene derivatives that are commonly used as acceptor material but that generally lack strong optical absorption coefficient.

Apart from fullrenes, small-molecules[12] such as perylene diimide derivatives, [13,14] polymers have attracted attention as acceptor materials. These acceptors offer advantages with respect to contributing more strongly to the absorption of visible or near-IR light. But the progress in this type of polymer:polymer solar cells are not comparable to polymer : fullrene cells in terms of efficiency.[15]

Another approach to design the acceptor polymers for solar cells was introduction of cyano groups to induce acceptor type behavior. The resulting solar cells made up of

this acceptor have resulted in a power conversion efficiency upto 1.7%. [16-19] In a another strategy, perylene diimides has been incorporated in the main chain [20-23] or as a pendant group [24] to make an acceptor polymer, but the resulting performance of a solar cells giving efficiency upto 1.5%.Also electron deficient, nitrogen heterocycles have been proposed to be used an acceptor materials for solar cells, for example, poly(pyridopyrazine vinylene)[25] or poly(quinoxaline vinylene).[26] Jenekhe and co-workers have poly(benzindazolebenzophenanthroline) [27,28] ladder polymers in bilayer cells as an acceptor materials. The most successful acceptor polymers for solar cells are alternating fluorenedithienylbenzothiadiazole (F8TBT) copolymers with an efficiency up to 1.8%.[29,30]. To design a successful acceptor polymer, it should have highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels that are correctly positioned with respect to the donor material used.

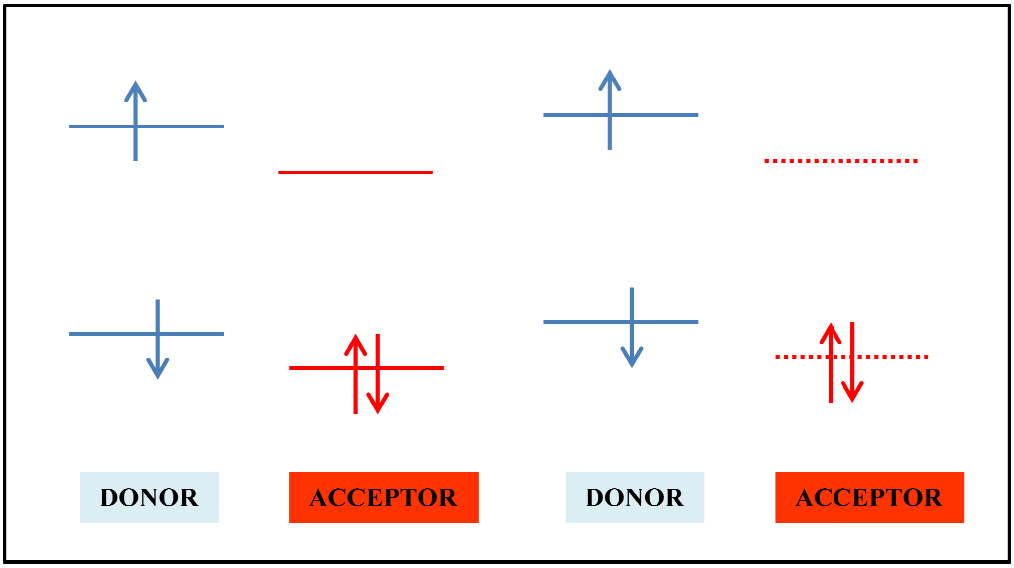


Figure 3.1 Energy levels for Donor and Acceptor materials. Dotted lines indicate tunable energy levels for acceptor

Here is the schematic representation for HOMO and LUMO energy levels for donor and acceptor material. (Figure 3.1) In the first diagram, the conventional donor-acceptor energy level diagram is shown. The most commonly used acceptor is Methanofullrene [6,6]-phenyl C_{61}-butyric acid methyl ester ($PC_{61}BM$). $PC_{61}BM$ is bulky in nature and segregates out while annealing P3HT-$PC_{61}BM$ blend due to mismatch in packing of these two materials. Also, the energy levels of $PC_{61}BM$ cannot be tuned, restricting use of many donor organic materials in solar cells. So it is important to develop new acceptor polymer which will have tunable energy levels which can facilitate use of different donors in conjunction with it. This is shown schematically in Fig. where acceptor energy levels are shown in dotted line indication that it can be tuned. Overall, it is essential to develop new π-conjugated acceptor polymers that have absorption spectrum with better overlap with solar emission spectrum and have good electron transport with tunable energy levels.

One of the ways to increase absorption of photons in visible region is to use two donor materials which will give good absorption in visible range. It leads to fabricating tandem solar cells wherein an additional hole conductor is used with in conjunction of donor and acceptor materials to broaden the absorption spectrum, thus in turn increasing efficiency of solar cell. It has been shown that, it can improve the efficiency of a solar cell but it is very difficult to obtain active layer morphology of both hole conductors with an acceptor molecule respectively. These are the reasons why, it is important to develop new π-conjugated acceptor polymers which can have broad absorption spectra, good electron mobility and tunable energy levels.

In this chapter, we have designed a strategy to synthesize a monomer for an acceptor polymer based on benzthiadiazole with the following aims:

1. Broad Absorption in Visible region
2. Tunable HOMO, LUMO levels
3. Good electron mobility

We have chosen to synthesize a polymer based on benzthiadiazole because it has been shown that when benzthiadiazole unit is used in different copolymers, it can give better absorption in visible region. So, it is of our interest to synthesize newly conjugated homopolymers and copolymers based on only benzthiadiazole as a repeating unit. There has been only one report regarding synthesis of homopolymer based on benzthiadiazole and also it was not fully characterized for solar cells application. One of the reason for this could be the homopolymer is very difficult to solubilize in common organic solvent restricting its use to form thin films. The other reason may be due lack of knowledge of synthesizing electron deficient polymers. Herewith, we came up with a strategy to synthesize the monomers and polymers, where we have incorporated different alkyl side chains which can solubilize the polymer in organic solvents. The monomers have designed in such a way that it will be soluble in common organic solvents and we have employed Suzuki polymerization conditions to obtain homopolymer and alternating polymer from these monomers.

3.2 Molecular Design and Synthesis

We have synthesized two monomers with different alkyl side chains (C_{14} and C_8). We synthesized the monomer for homopolymer and alternation copolymer from readily

available catechol which was converted to Compound 1 by Williamson synthesis. This is followed by nitration of Compound 1 by using HNO_3 and CH_3COOH to give di-nitro derivative Compound 2. The nitro groups are reduced to give Compound 3 using $SnCl_2$ and HCl, followed by thiadiazole ring formation using thionyl chloride ($SOCl_2$) and triethylamine.(Compound 4). The Monomer M1 is synthesized from Compound 4 by electrophilic substitution reaction using bromine and acetic acid.(Figure 3.2)

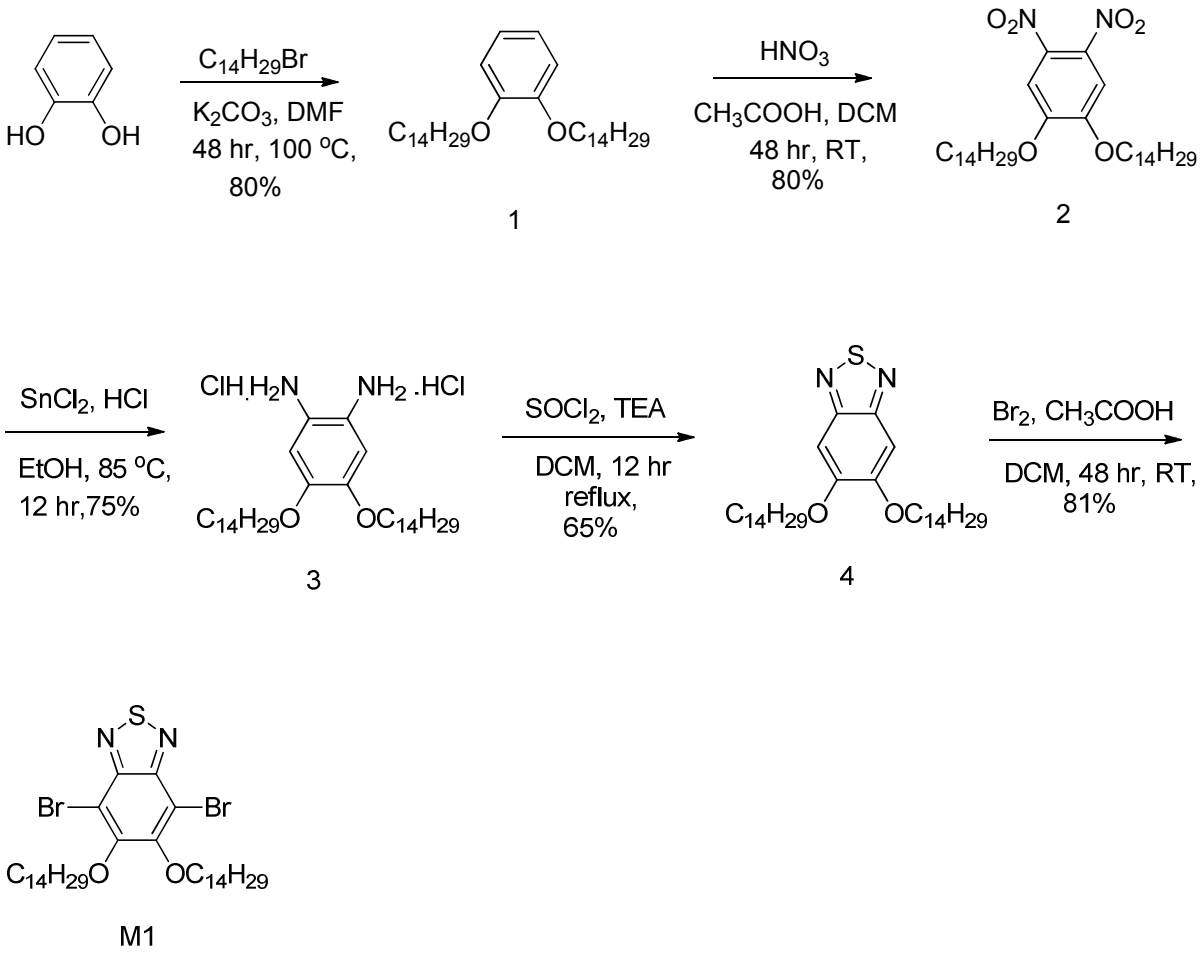


Figure 3.2 Synthesis Scheme for Monomer 1(M1) used for making PBTD & PBTDV polymers

It is confirmed from ^{1}H and ^{13}C NMR that Monomer 1 is pure and further used for polymerization. The Suzuki polymerization is carried out using Pd $(tBu_3P)_2$ catalyst and LiOH as a base in mixture of solvents (n-butyl ether, tetrahydrofuran and ortho dichlorobenzene) to yield PBTD 1. The synthetic scheme for this polymer is shown below in Figure 3.3.

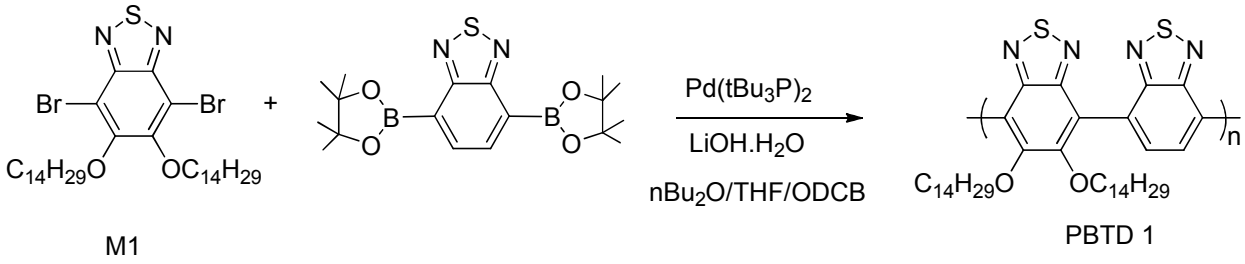
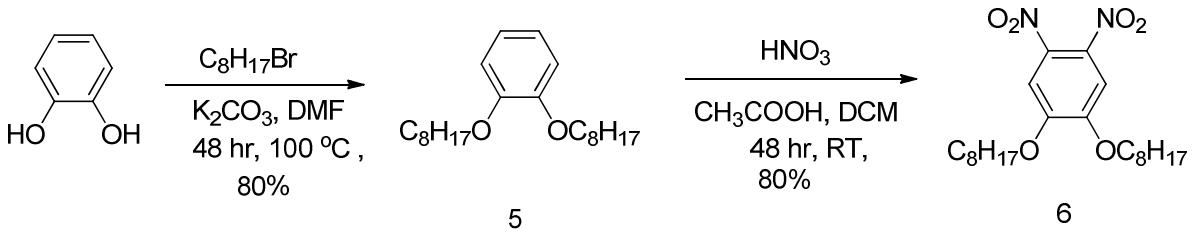


Figure 3.3 Synthesis of Polymer PBTD 1 from M1

The polymerization is carried out for 7 days. The molecular weight of polymer is found by GPC (Mn = 66.7 KDa, n=96). We are also interested to see whether we can tune energy levels of polymer by changing side chains on polymeric unit. It is well known from DV group research that the side chains can affect optical and electronic properties of polymers. So, we have designed another monomer with C8 alkyl chain length and synthesized the monomer as shown in the scheme below.(Figure 3.4)



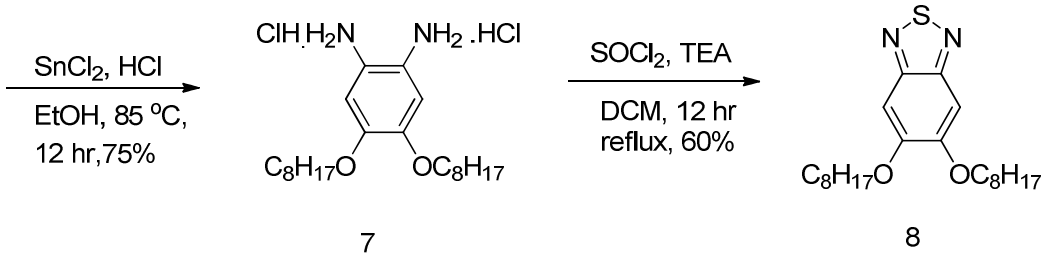


Figure 3.4 Synthesis Scheme for Compound 5-8

The overall synthesis is similar to Monomer 1. Catechol was converted to Compound 5 by Williamson synthesis using octyl bromide. This is followed by electrophilic substitution reaction using HNO_3 and CH_3COOH to give di-nitro product (Compound 6). The nitro groups are reduced to yield Compound 7 using $SnCl_2$ and HCl, followed by thiadiazole ring formation using thionyl chloride ($SOCl_2$) and triethylamine. (Compound 8).It has been observed that during the synthesis of polymers from Monomer 1 that synthesis of electron deficient polymers is very prolong process which takes 7 days to form a polymer. It is well known that Suzuki polymerization of iodo compounds goes faster than that of bromo analogues. Hence, we have decided to incorporate iodide instead of bromide expecting that the polymerization will go faster as compared to the previous one. So, we did iodination of compound 7 using following protocol.(Figure 3.5)

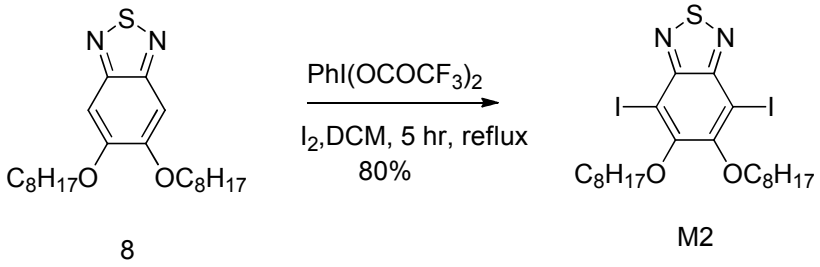
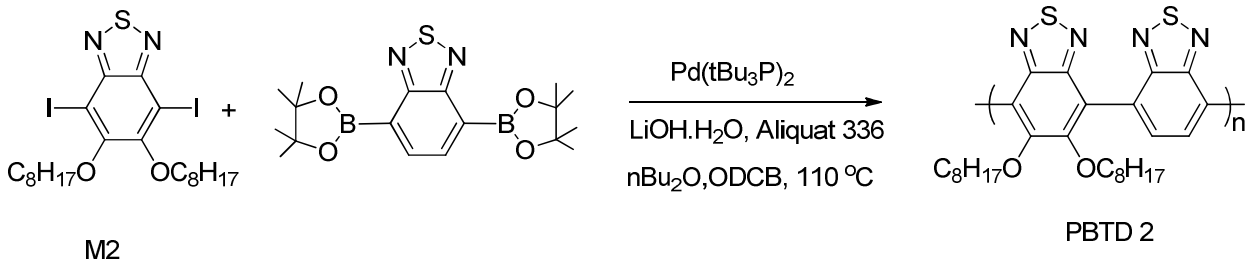


Figure 3.5 Iodination of Compound 8

The Suzuki polymerization is carried out of Monomer M2 using Pd ($tBu_3P)_2$ catalyst and LiOH as a base in mixture of solvents (n-butyl ether, tetrahydrofuran and ortho dichlorobenzene) to yield PBTD 2.(Figure 3.6)



M2 PBTD 2

Figure 3.6 Synthesis of Polymer PBTD 2 from M2

3.3 Characterization of Monomers

All the compounds were characterized by using ^{1}H NMR. NMRs for monomers are shown below. The NMR for Monomer 1 (Figure 3.8) indicates pure compound indicating 54 protons in alkyl region (0.86-1.92 ppm). The peak at 4.14-4.18 ppm indicates 4 protons next to oxygen in alkyl chains and deshielded. The NMR for Monomer 2 (Figure 3.9) indicates pure compound indicating 30 protons in alkyl region (0.87-1.94 ppm). The peak at 4.11-4.14 ppm indicates 4 protons next to oxygen in alkyl chains because of deshielding effect.

3.4 UV-vis Studies and Cyclic Voltametry

The absorption spectra of PBTD 1 and PBTD 2 are recorded by casting a thin film of these polymers from chloroform solution. The UV spectra does not show any

significant absorption in visible range (only 280-400 nm) before and after thermal annealing at 100 ^{o}C for 30 min, indicating that these homopolymers may not be a good choice as an acceptor polymers which can absorb in visible region. PBTD 1 and PBTD 2 have similar absorption spectra indicating that side chain has very little effect on optical properties of these polymers.

Cyclic voltametry is carried out to investigate the effect of side chains on energy levels of the homopolymers. It has been observed that the different side chains of the polymer affects the oxidation and reduction potentials in cyclic voltametry resulting into different HOMO and LUMO energy levels for these homopolymers. Following table provides the information for HOMO and LUMO energy levels for PBTD 1 and PBTD 2 along with method of polymerization and molecular weights of polymers.

Polymer	**Method of Polymerization**	**Mn(KDa)**	**Energy Levels measured by CV (eV)**	
			HOMO	**LUMO**
PBTD 1	Suzuki Polymerization	66.7	-5.64	-2.93
PBTD 2	Suzuki Polymerization	15.2	-5.71	-3.03

Table 3.1 Molecular weight and Energy levels for Polymer PBTD 1 and PBTD 2

The above values indicate that HOMO and LUMO levels of the polymers can be tuned by changing the side chains of the polymer. In this case, it has been observed that

HOMO and LUMO values for PBTD 2 are lower than PBTD 1. This explores an opportunity of use of different donor molecules in conjunction with these acceptor polymers. So it is important to design a polymer with good optical properties which can in turn give efficient solar cell.

We believe that one of the reason low absorption in Homopolymers could be side chain interactions between adjacent repeating units of Homopolymers. Therefore, we have decided to synthesize a conjugated polymer with conjugated spacer in between the repeating units, so that the side chain might not interfere with each other and it may enhance the optical properties of the polymer. To incorporate a conjugated spacer between repeating unit of a polymer, we synthesized alternating copolymers of Monomer 1 and Monomer 2 using Stille polymerization. The synthesis protocol for polymerization is shown below in Figure 3.7.

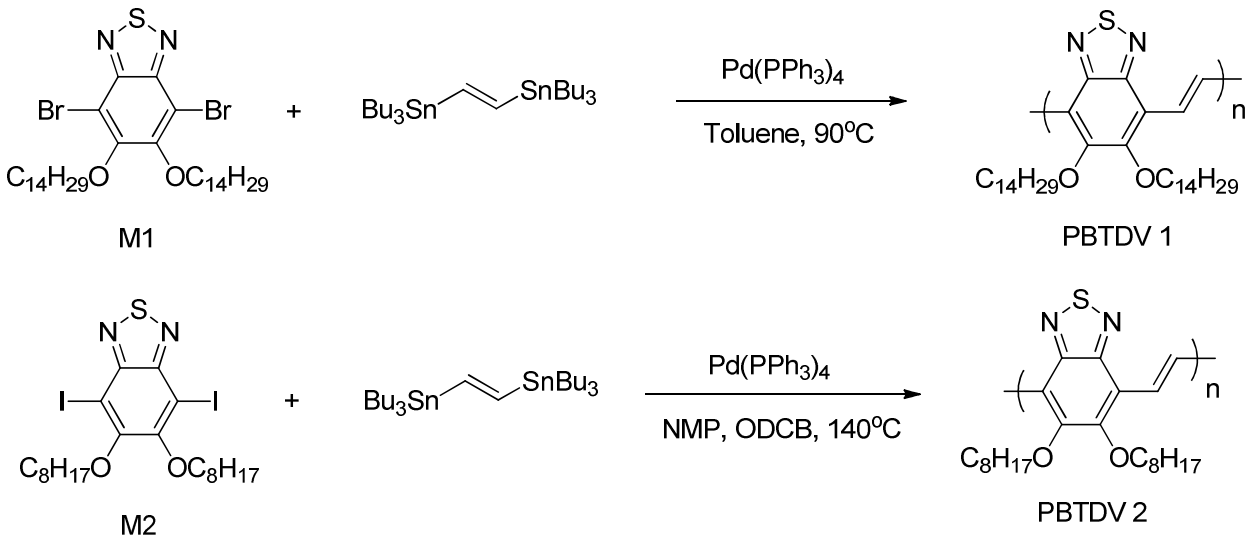


Figure 3.7 Synthesis of Polymer PBTDV 1 and PBTDV 2

PBTDV 1 is synthesized using $Pd(PPh_3)_4$ as a catalyst and toluene as a solvent and heated to 90^oC for 5 days. The resulting copolymer has molecular weight of 10.7 KDa. PBTDV 2 is synthesized using Pd $(PPh_3)_4$ as a catalyst and NMP and ODCB as solvents and heated to 140 ^oC for 5 days which has resulted into molecular weight of 9.1 KDa. The polymerization procedures are explained in detail in the experimental section.

3.5 Characterization of Alternating Copolymers

3.5.1 UV-Vis Absorption Studies and Cyclic voltametry

The absorption spectra of PBTDV 1 and PBTDV 2 are recorded by casting a thin film of these polymers from chloroform solution. The UV-vis spectra show broad absorption spectra indicating that the conjugated spacer has an important role in designing the polymer to get good optical properties. These polymers can absorb from 280-740nm in visible region. Both PBTDV 1 and PBTDV 2 have similar absorption indicating that different side chain has no effect on optical properties of these polymers.

Polymer	**Method of Polymerization**	**Mn(KDa)**	**Energy Levels measured by CV in (eV)**	
			HOMO	**LUMO**
PBTDV 1	Stille Polymerization	10.7	-5.45	-3.77
PBTDV 2	Stille Polymerization	9.1	-5.24	-3.54

Table 3.2 Molecular weight and Energy levels for Polymer PBTDV 1 and PBTDV 2

Cyclic voltametry studies have shown that there are different HOMO and LUMO energy levels for these Alternating Copolymers depending on the side chains. Following table provides the information for HOMO and LUMO energy levels for PBTDV 1 and PBTDV 2.

3.5.2 Mobility Studies

Time of flight mobility studies are under investigation for all the polymers. We measured time of flight mobility for PBTDV 1 and it has been observed that the mobility of this polymer is 10^{-3} cm^2/Vs which is comparable to PCBM in thin films. This indicates that these polymers have comparable electron mobilities as PCBM and potentially be used to efficient solar cells. The mobility studies for other Homopolymers and Copolymers are under investigation.

3.6 Future work and directions

P3HT/PCBM bulk heterojunction morphological properties are extensively studied to device a solar cells. We have synthesized a new acceptor polymer which has tunable energy levels and broad absorption in visible region. So, the next challenge is to study the morphology of these polymers with different donor and optimization of morphology to give higher efficient solar cells. One of the main ongoing researches in DV research group is to synthesize conjugated nanoparticles and assemble it into different morphologies to get higher efficient solar cells. One can synthesize these acceptor nanoparticles and assemble with P3HT nanoparticles to assemble these materials into different morphologies by using sphere packing. The other way is most common way of

mixing these acceptor polymers in conjuction with different donor polymers to optimize the morphology to get a bulk heterojunction.

3.7 Experimental Details

All chemicals were purchased from commercial sources (Acros, Aldrich, Alfa Aesar, TCI, and Strem) and used without further purification, unless otherwise noted. THF was distilled from sodium-benzophenone ketyl. NBS was recrystallized from water. Common solvents were purchased from EMD (through VWR). Routine monitoring of reactions was carried out on glass-supported EMD silica gel 60 F_{254} TLC plates. Flash chromatography was performed using silica gel from Sorbent Technologies (Standard Grade, 60 Å, 32-63 μm). All ^{1}H and ^{13}C $\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance400 spectrometer, unless otherwise noted. Chemical shifts and coupling constants (*J*) are reported in parts per million (δ) and Hertz, respectively. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. Chloroform-D ($CDCl_3$) contained 0.05% v/v tetramethylsilane (TMS) and Chloroform-D peak was set to 7.26 ppm on all proton spectra.

In Gel permeation chromatography (GPC) was done in the NSF-sponsored Materials Research Science and Engineering Center on Polymers (MRSEC) at the University of Massachusetts Amherst. GPC analyses were performed on a Polymer Laboratories GPC50 integrated system with DMF (1.0 mL/min, 120 °C) elution, 3 x Mixed C (300 x 7.5 mm) columns, and RI detection. Molecular weights were obtained based on PMMA standards, with toluene as the flow rate marker, and may be overestimated by a factor of 1.5-2.0.

UV-vis absorption spectra were measured with a Shimadzu UV 3600PC spectrometer Polymer-Based Materials Harvesting Solar Energy (Energy Frontier Research Center at the University of Massachusetts Amherst)EFRC laboratory. Stock solutions of polymers (*c*=1mg/10mL) were prepared in spectrophotometric grade chloroform (Fisher, Optima). UV–vis experiments for thin films were done by spin casting (1400 rpm) of 1 wt % solution of polymer in chloroform on a glass plate. Similarly, to the 1 wt % solution of polymer in chloroform PCBM (1:1 wt% with respect to polymer) was added and spin casted (600 rpm) onto a glass plate. These films were annealed at 100°C for 30 minutes, UV-Vis and Fluorescence spectra were recorded before and after annealing. Fluorescence spectra were measured on PTA flourimeter for thin films & on JASCO FP-6500 spectrofluorometer for solutions studies. Cyclic Voltammetry studies were done using BAS CV- 50 W instrument. Stock solutions of polymer (1wt% polymer in chloroform) were prepared & films are spin casted on the platinum working electrode CV was recorded with tetrabutylammonium hexfluorophosphate as a supporting electrolyte (0.1M) in acetonitrile. The redox potentials were determined versus an Ag/Ag^+ reference electrode.The working and auxiliary electrodes were cleaned after each run. HOMO and LUMO values were calculated using Fc/Fc^+ as a reference.

1,2-bis(tetradecyloxy)benzene (1). To a solution of catechol (5 g, 0.045 mol) in dry DMF (25mL) was added 1-bromotetradecane (0.104 mol, 31mL) and K_2CO_3 (18.82 g, 0.135 mol). The mixture was stirred at 100°C under a nitrogen atmosphere for 40 hours. After cooling the mixture to room temperature (RT), 50mL of water were added. The organic layer was separated and the aqueous layer was extracted with DCM. The

combined organic phase was dried over $MgSO_4$. After filtration, the mixture was concentrated under vacuum. The product was recrystallized twice from acetone. Yield: 17.5 g (85%), white needlelike crystals. ^{1}H NMR ($CDCl_3$): δ = 6.91 (s, 4H), 3.99-4.03 (t, J = 6.6 Hz, 4H), 1.88 – 1.81 (m, 4H), 1.52 – 1.15 (m, 44H), 0.94-0.90 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ = 149.30, 121.30, 114.13, 69.28, 32.01,31.84, 29.79, 29.75, 29.72, 29.53, 29.45, 26.14, 22.76, 14.16.

1,2-dinitro-4,5-bis(tetradecyloxy)benzene (2). To a two neck round-bottom flask containing dichloromethane (100mL), acetic acid (100mL), and 1,2-bisdodecyloxybenzene (5 g, 9.95 mmol) cooled to 10°C was added dropwise 69% nitric acid (150mL). The mixture was allowed to warm to room temperature and the mixture was stirred for 40 hours. After completion of the reaction, the reaction mixture was poured into ice-water and the dichloromethane layer separated. The water phase was extracted with dichloromethane. The combined organic phase was washed with water, sat. $NaHCO_3$ (aq), brine and dried over $MgSO_4$. Concentration in vacuum gave the crude product that was recrystallized from ethanol. Yield: 10.57 g (90%), yellow solid. ^{1}H NMR ($CDCl_3$): δ = 7.29 (s, 2H), 4.10 (t, J = 6.5 Hz, 4H), 1.90 – 1.83 (m, 4H), 1.51 – 1.26 (m, 44H), 0.88 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ = 151.81, 136.43, 107.89, 70.22, 31.93, 29.73, 29.60, 29.55, 29.40, 29.26, 28.72, 28.53, 22.71, 14.11.

4,5-bis(tetradecyloxy)benzene-1,2-diaminium chloride (3). A mixture of 1,2-dinitro-4,5-bis-(tetradecyloxy)-benzene (2g, 3.37mmol) and $Sn(II)Cl_2$ (26.9mmol, 5.1g) in ethanol (50mL) and conc. HCl (20mL) was heated to 85 ^{o}C over the night. After cooling to room temperature the product was filtered and washed with water and methanol.

Finally it was dried at RT under a stream of argon and used directly (unstable). Yield: 1.5 g (73%), off-white solid.

5,6-bis(tetradecyloxy)benzo[*c*][1,2,5]thiadiazole (4). To a mixture of 4,5-bis(tetradecyloxy)-benzene-1,2-diaminium chloride (1.54g, 2.54mmol) and triethylamine (25.1mmol, 3.5mL) in 40mL dichloromethane was slowly added a solution of thionyl chloride (4.83 mmol, 0.352mL) in 5mL dichloromethane. After addition the mixture was heated to reflux for 6 hours. The cooled solution was concentrated in vacuum followed by trituration in water. After stirring for 30 min the product was filtered and recrystallized from ethanol. Yield: 0.77 g (65 %), off-white solid. ^{1}H NMR ($CDCl_3$): δ = 7.12 (s, 2H), 4.08 (t, J = 6.5 Hz, 4H), 1.95 – 1.85 (m, 4H), 1.51 – 1.25 (m, 44H), 0.89 – 0.85 (m, 6H). ^{13}C NMR ($CDCl_3$): δ = 154.17, 151.40, 98.44, 69.13, 31.92, 29.71, 29.69, 29.66, 29.61, 29.36, 28.75, 26.02, 22.68, 14.09.

4,7-dibromo-5,6-bis(tetradecyloxy)benzo[*c*][1,2,5]thiadiazole (M1). To a solution of **3** (1.07 g, 1.90 mmol) in a mixture of dichloromethane (50 mL) and acetic acid (22mL) was added bromine (0.70 mL, 13.35 mmol), and the resulting mixture was stirred in the dark for 48 h at room temperature. The mixture was then poured in water (75mL), extracted with dichloromethane, sequentially washed with water, saturated $NaHCO_3$ (aq), 1M Na_2SO_3 (aq) and the solvents are evaporated under reduced pressure. The crude product was purified by recrystallization from ethanol twice to give fluffy needle-like microcrystals. Yield: 0.95 g (75%). ^{1}H NMR ($CDCl_3$): δ = 4.16 (t, J = 6.6 Hz, 4H), 1.92 – 1.85 (m, 4H), 1.62 – 1.46 (m, 4H), 1.46 – 1.19 (m, 40H), 0.88 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ = 154.52, 150.38, 106.27, 75.16, 31.94, 30.28, 29.72, 29.70, 29.69, 29.65, 29.63, 29.45, 29.39, 29.27, 26.00, 22.71, 14.13.

1,2-bis-octyloxy-benzene (5). To a solution of catechol (15 g, 0.136 mol) in dry DMF (75 mL) was added 1-bromooctane (0.34mol, 59.2mL) and K_2CO_3 (56.5 g, 0.408 mol). The mixture was stirred at 100 °C under a nitrogen atmosphere for 40 hours. After cooling the mixture to room temperature (RT), 150 mL of water were added. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic phase was dried over $MgSO_4$. After filtration, the mixture was concentrated under vacuum. Purification of the residue by silica gel chromatography (10:90 EtOAc: hexanes) afforded **5** as colorless oil Yield: 35.5 g (78%), colorless liquid.^{1}H NMR ($CDCl_3$): δ = 6.89 (s, 4H), 3.99 (t, J = 6.6 Hz, 4H), 1.85 – 1.78 (m, 4H), 1.57 – 1.22 (m, 20H), 0.89 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ = 149.38, 121.12, 114.23, 69.40, 31.98, 29.55, 29.49, 29.44, 26.20, 22.82, 14.24.

1,2-dinitro-4,5-bis-octyloxy-benzene (6). To a two neck round-bottom flask containing dichloromethane (420 mL), acetic acid (420mL), and 1,2-bis-octyloxy-benzene(35 g, 0.104 mol) cooled to 10 °C was added dropwise 69% nitric acid (550 mL). The mixture was allowed to warm to room temperature and the mixture was stirred for 40 hours. After completion of the reaction, the reaction mixture was poured into ice-water and the dichloromethane layer separated. The water phase was extracted with dichloromethane. The combined organic phase was washed with water, sat. $NaHCO_3$ (aq), brine and dried over $MgSO_4$. Concentration in vacuum gave the crude product that was recrystallized from ethanol. Yield: 36 g (81%), yellow solid. ^{1}H NMR ($CDCl_3$): δ = 7.29 (s, 2H), 4.09 (t, J = 6.5 Hz, 4H), 1.90 – 1.82 (m, 4H), 1.51 – 1.28 (m, 20H), 0.88 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ = 151.93, 136.55, 108.01, 70.31, 31.87, 29.30, 28.81, 25.92, 22.75, 14.18.

4,5-bis(octoloxy)benzene-1,2-diaminium chloride (7). A mixture of 1,2-dinitro-4,5-bis-octyloxy-benzene (10 g, 0.0235 mol) and Sn(II)Cl_2 (0.188 mmol, 42.5 g) in ethanol (350 mL) and conc. HCl (140mL) was heated to 85 ^{o}C over the night. After cooling to room temperature the product was filtered and washed with water and methanol. Finally it was dried at RT under a stream of argon and used directly (unstable). Yield: 19.95 g (95%), off-white solid.

5,6-bis-octyloxy-benzo[1,2,5]thiadiazole (8). To a mixture of 4,5-bis(octoloxy)benzene-1,2-diaminium chloride (10g, 0.0228 mmol) and triethylamine (0.0228 mmol, 32.1mL) in 380mL dichloromethane was slowly added a solution of thionyl chloride (0.0457 mmol, 3.3mL) in 47mL dichloromethane. After addition the mixture was heated to reflux for 6 hours. The cooled solution was concentrated in vacuum followed by trituration in water. After stirring for 30 min the product was filtered and reprecipitated from ethanol. Purification of the residue by silica gel chromatography (10:90 EtOAc: hexanes) afforded **8** as off-white solid. 9.0g (60 %), ^{1}H NMR ($CDCl_3$): δ = 7.13 (s, 2H), 4.09 (t, J = 6.5 Hz, 4H), 1.94 – 1.87 (m, 4H), 1.53 – 1.29 (m, 20H), 0.90 – 0.87 (m, 6H). ^{13}C NMR ($CDCl_3$): δ = 154.29, 151.54, 98.55, 69.28, 31.95, 29.47, 29.41, 28.88, 26.16, 22.82, 14.25.

4,7-Diiodo-5,6-bis-octyloxy-benzo[1,2,5]thiadiazole (M2). In a round bottom flask, 5,6-bis-octyloxy-benzo[1,2,5]thiadiazole (1g, 2.547 mmol), iodine (0.775g, 3.056 mmol), and PhI($OCOCF_3$)$_2$ were added along with 60mL dichloromethane. The reaction mixture was refluxed for 5h. After 5h, sodium thiosulphate solution (100mL) was added to reaction mixture and stirred further for 1h. Water (100mL) was added to it and extracted with DCM (4x50mL). The organic layer was washed with $NaHCO_3$ (100mL) and sat.NaCl (100mL) solution and dried over $MgSO_4$. Purification of the residue by silica gel

chromatography (40:60 DCM: hexanes) afforded **M2** as light yellow solid. Yield:-1.35g (82%).^{1}H NMR ($CDCl_3$): δ = 4.12 (t, J = 6.5 Hz, 4H), 1.94 – 1.87 (m, 4H), 1.58 – 1.30 (m, 20H), 0.91 – 0.87 (m, 6H). ^{13}C NMR ($CDCl_3$): δ = 157.24, 151.96, 82.80, 75.10, 31.99, 30.51, 29.59, 29.43, 26.28, 22.82, 14.26.

Polymer PBTD 1

Monomer M1 (250 mg, 0.347 mmol) and catalyst $Pd(tBu_3P)_2$ (17.7 mg, 0.0347 mmol) are taken into the Schlenk flask in the glove box under argon atmosphere. The solvents n-butyl ether (nBu2O) and ortho-dichlorobenzene (ODCB) (4 mL total) and THF (4 mL) are taken into another Schlenk flask and degassed by freeze pump thaw technique for 3 times. This solution is added to aliquat 336 (12 drops) under argon atmosphere and deoxygenated the solution by bubbling argon into it for 30 minutes. This solution is added to Schlenk flask containing Monomer 1 and catalyst under argon atmosphere. Deoxygenated aq.LiOH (2.6 mL) is subsequently added to Schlenk flask containing all other reagents and Schlenk flask was immsered in a preheated oil bath of 110^{o}C. The reaction is carried out for 7 days maintaining temperature of reaction mixture. After 7 days, the reaction mixture was precipitated in ice-cold methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, EtOAc, ether and $CHCl_3$. The $CHCl_3$ fraction, after concentration under reduced pressure, afforded 170 mg of the polymer. The material isolated from the hexanes fraction was analyzed by GPC.

Polymer PBTD 2

Monomer M2 (404 mg, 0.626 mmol) and catalyst $Pd(tBu_3P)_2$ (32.02mg, 0.0626 mmol) are taken into the Schlenk flask in the glove box under argon atmosphere. The solvents n-butyl ether (nBu2O) and ortho-dichlorobenzene (ODCB) (12 mL total) are taken into another Schlenk flask and degassed by freeze pump thaw technique for 3 times. 3mL of this solution is added to aliquat 336 (20 drops) under argon atmosphere and deoxygenated the solution by bubbling argon into it for 30 minutes. This solution is added to Schlenk flask containing Monomer 1 and catalyst under argon atmosphere. Deoxygenated aq.LiOH (3.6 mL) is subsequently added to Schlenk flask containing all other reagents and Schlenk flask was immsered in a preheated oil bath of 110^{o}C. The reaction is carried out for 7 days maintaining temperature of reaction mixture. After 7 days, the reaction mixture was precipitated in ice-cold methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, EtOAc, hexanes and $CHCl_3$. The $CHCl_3$ fraction, after concentration under reduced pressure, afforded 91 mg of the polymer. The material isolated from the hexanes fraction was analyzed by GPC.

Polymer PBTDV 1

Monomer M1 (210 mg, 0.0.292 mmol) and catalyst $Pd(PPh_3)_4$ (33.7mg, 0.0292 mmol) are taken into the Schlenk flask in the glove box under argon atmosphere. The toluene (10 mL) is taken into another Schlenk flask and degassed by freeze pump thaw technique for 3 times. Approximately 5 mL of Toluene is taken into another flask and ethylene ditin compound is added to it and deoxygenated the solution by bubbling argon into it for

30 minutes. This solution is added to Schlenk flask containing Monomer 1 and catalyst under argon atmosphere along with remaining 5 mL of toluene. The Schlenk flask is immsered in a preheated oil bath of 90^{o}C. The reaction is carried out for 5 days maintaining temperature of reaction mixture. After 5 days, the reaction mixture was precipitated in ice-cold methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, acetone and $CHCl_3$. The $CHCl_3$ fraction, after concentration under reduced pressure, afforded 180 mg of the polymer. The material isolated from the hexanes fraction was analyzed by GPC.

Polymer PBTDV 2

Monomer M2 (400mg, 0.0.620 mmol) and catalyst $Pd(PPh_3)_4$ (71.7 mg, 0.062 mmol) are taken into the Schlenk flask in the glove box under argon atmosphere. The solvents NMP and ODCB (1:2) (20 mL total) is taken into another Schlenk flask and degassed by freeze pump thaw technique for 3 times. Approximately 3 mL of solvent (NMP/ODCB) is taken into another flask and ethylene ditin compound is added to it and deoxygenated the solution by bubbling argon into it for 40 minutes. This solution is added to Schlenk flask containing Monomer 1 and catalyst under argon atmosphere along with remaining solvent. The Schlenk flask is immsered in a preheated oil bath of 140^{o}C. The reaction is carried out for 5 days maintaining temperature of reaction mixture. After 5 days, the reaction mixture was precipitated in ice-cold methanol. The polymer was transferred to an extraction thimble and fractionated via Soxhlet extraction with MeOH, acetone, ethyl acetate and $CHCl_3$. The $CHCl_3$ fraction, after concentration under reduced pressure, afforded 150 mg of the polymer. The material isolated from the hexanes fraction was analyzed by GPC.

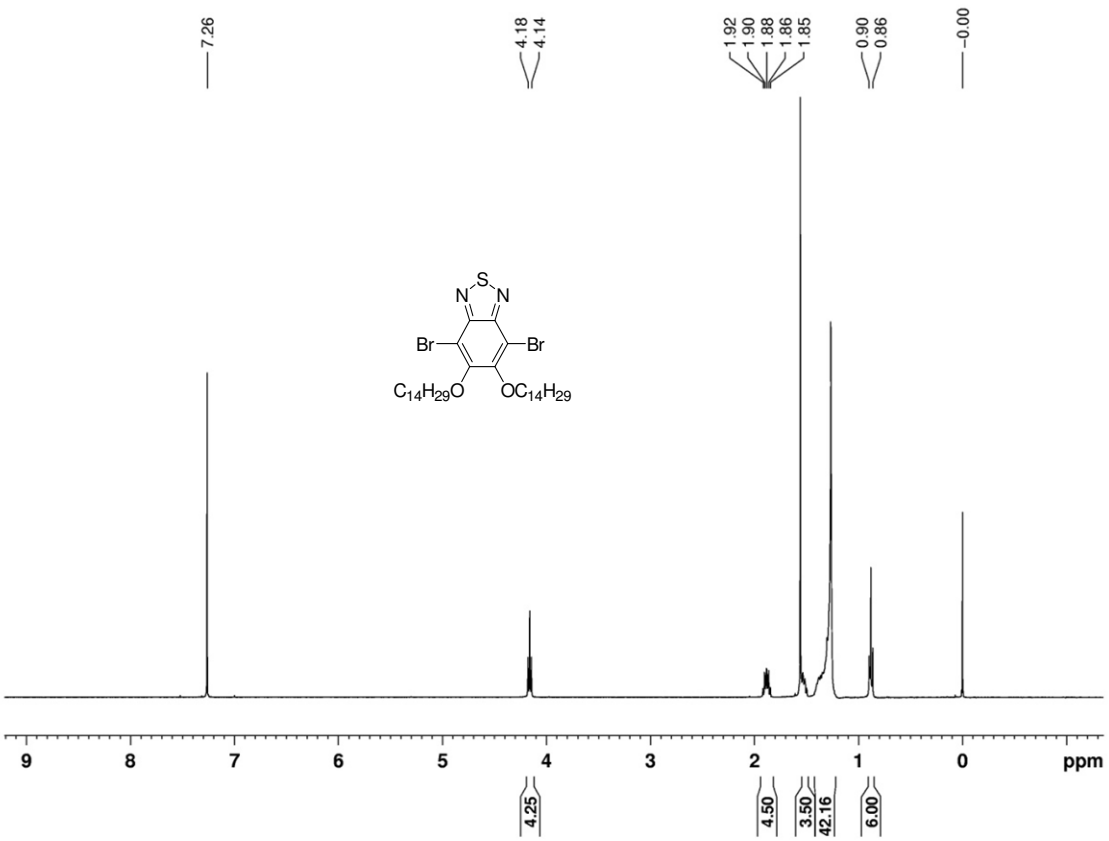


Figure 3.8 ^{1}H NMR of Monomer M1

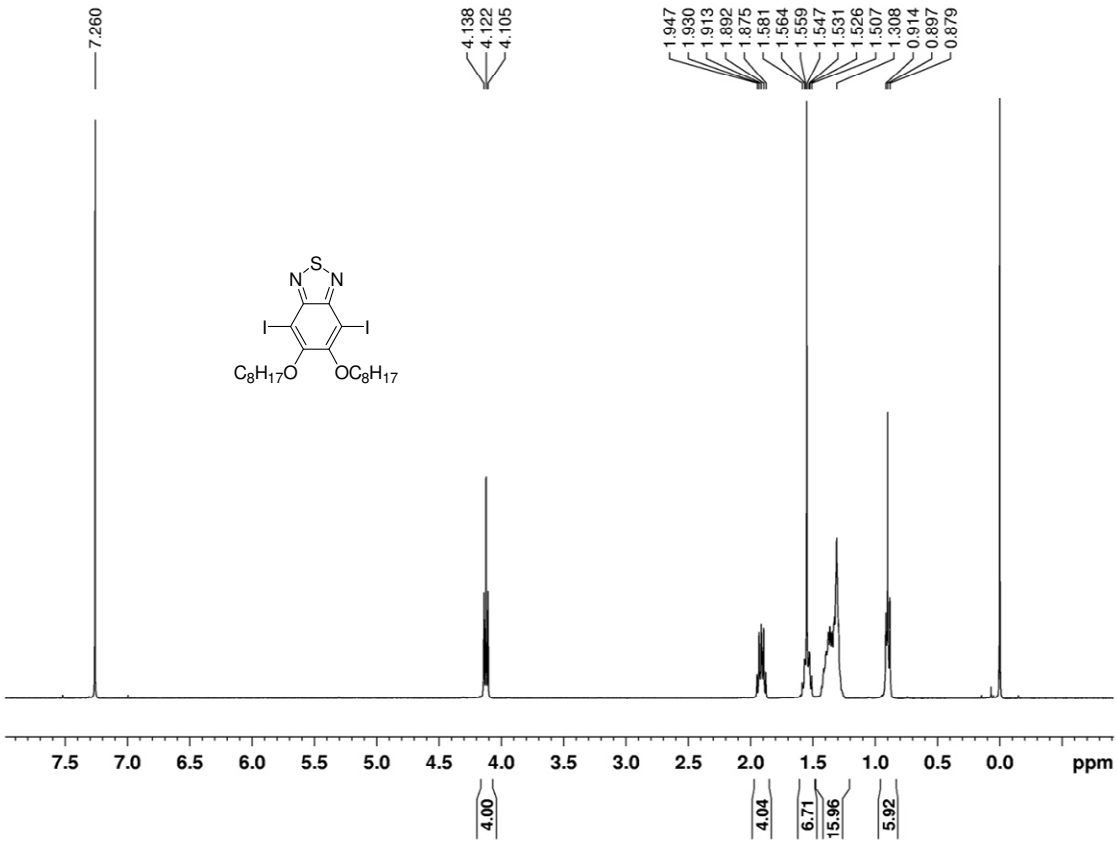


Figure 3.9 ^{1}H NMR of Monomer M2

3.8. References

1. Brabec, C. J.; Durrant, J. R., "Solution processed organic solar cells", *MRS Bulletin* **2008**, *33*, 670.

2. Janssen, R. A. J.; Hummelen, J. C.; Sariciftci, N. S., "Polymer- fullrene bulk heterojunction solar cells", *MRS Bulletin* **2005**, *30*, 33.

3. Thompson, B. C.; Frechet, J. M. J., "Polymer- fullrene composite solar cells", *Angewandte Chemie International Edition* **2008**, *47*, 58.

4. Dennler, G.; Scharber, M. C.; Brabec, C. J., "Polymer-fullrene bulk heterojunction solar cells" *Advanced Materials* **2009**, *21*, 1323.

5. Boudreault, P. L. T.; Najari, A.; Leclerc, M., "Processable low band gap polymers for photovoltaic applications", *Chemistry of Materials* **2011**, *23*, 456–469.

6. Liang, Y.; Yu, L., "New Class of Semiconducting Polymers for Bulk Heterojunction Solar Cells with Exceptionally High Performance", *Account of Chemical Research* **2010**, *43*, 1227.

7. Chen, J.; Cao, Y., "Development of Novel Conjugated Donor Polymers for High-Efficiency Bulk-Heterojunction Photovoltaic Devices", *Account of Chemical Research* **2009**, *43*, 1709.

8. Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J., "Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions", *Science* **1995**, *270*, 1789.

9. Wienk, M. M.; Kroon, J. M.; Verhees, W. J. H.; Knol, J.; Hummelen, J. C.; van Hal, P. A.; Janssen, R. A. J., "Efficient Methano[70]fullerene/MDMO-PPV Bulk Heterojunction Photovoltaic Cells", *Angewandte Chemie International Edition* **2003**, *42*, 3371.

10. Mihailetchi, V. D.; van Duren, J. K. J.; Blom, P. W. M.; Hummelen, J. C.; Janssen, R. A. J.; Kroon, J. M.; Rispens, M. T.; Verhees, W. J. H.; Wienk, M. M., "Electron Transport in a Methanofullerene", *Advanced Functional Materials* **2003**, *13*, 43.

11. Yang, X.; van Duren, J. K. J.; Rispens, M. T.; Hummelen, J. C.; Janssen, R. A. J.; Michels, M. A. J.; Loos, J., "Crystalline Organization of a Methanofullerene as Used for Plastic Solar-Cell Applications", *Advanced Materials* **2004**, 16, 802.

12. Brunetti, F. G.; Gong, X.; Tong, M.; Heeger, A. J.; Wudl, F., "Strain and Hückel Aromaticity: Driving Forces for a Promising New Generation of Electron Acceptors in Organic Electronics", *Angewandte Chemie International Edition* **2010**, 49, 532.

13. Dittmer, J. J.; Marseglia, E. A.; Friend, R. H., "Electron Trapping in Dye/Polymer Blend Photovoltaic Cells", *Advanced Materials* **2000**, 12, 1270.

14. Schmidt-Mende, L.; Fechtenkotter, A.; M€ullen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D., "Self-Organized Discotic Liquid Crystals for High-Efficiency Organic Photovoltaics", *Science* **2001**, *293*, 1119.

15. McNeill, C. R.; Greenham, N. C., "Conjugated-Polymer Blends for Optoelectronics", *Advanced Materials* **2009**, *21*, 3840.

16. Yu, G.; Heeger, A. J., “Charge separation and photovoltaic conversion in polymer composites with internal donor/acceptor heterojunctions”, *Journal of Applied Physics* **1995**, *78*, 4510.

17. Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B., “Efficient photodiodes from interpenetrating polymer networks”, *Nature* **1995**, *376*, 498.

18. Veenstra, S. C.; Verhees, W. J. H.; Kroon, J. M.; Koetse, M. M.; Sweelssen, J.; Bastiaansen, J. J. A. M.; Schoo, H. F. M.; Yang, X.; Alexeev, A.; Loos, J.; Schubert, U. S.; Wienk, M. M., “Photovoltaic Properties of a Conjugated Polymer Blend of MDMO−PPV and PCNEPV”, *Chemistry of Materials* **2004**, *16*, 2503.

19. Kietzke, T.; Horhold, H.-H.; Neher, D., “Efficient Polymer Solar Cells Based on M3EH−PPV”, *Chemistry of Materials* **2005**, *17*, 6532.

20. Neuteboom, E. E.; Meskers, S. C. J.; van Hal, P. A.; van Duren, J. K. J.; Meijer, E. W.; Janssen, R. A. J.; Dupin, H.; Pourtois, G.; Cornil, J.; Lazzaroni, R.; Bredas, J. L.; Beljonne, D., “Alternating Oligo(*p*-phenylene vinylene)−Perylene Bisimide Copolymers: Synthesis, Photophysics, and Photovoltaic Properties of a New Class of Donor−Acceptor Materials”, *Journal of American Chemical Society* **2003**, *125*, 8625.

21. Zhan, X.; Tan, Z.; Domercq, B.; An, Z.; Zhang, X.; Barlow, S.; Li, Y.; Zhu, D.; Kippelen, B.; Marder, S. R., “A High-Mobility Electron-Transport Polymer with Broad Absorption and Its Use in Field-Effect Transistors and All-Polymer Solar Cells”, *Journal of American Chemical Society* **2007**, *129*, 7246.

22. Hou, J.;Zhang, S.;Chen,T.L.;Yang,Y., "A new n-type low bandgap conjugated polymer P-co-CDT: synthesis and excellent reversible electrochemical and electrochromic properties", *Chemical Communications* **2008**, 6034.

23. Huo, L.; Zhou, Y.; Li, Y., "Synthesis and Absorption Spectra of n-Type Conjugated Polymers Based on Perylene Diimide", *Macromolecular Rapid Communications* **2008**, *29*, 1444.

24. Palermo, V.; Otten, M. B. J.; Liscio, A.; Schwartz, E.; de Witte, P. A. J.; Castriciano, M. A.; Wienk, M. M.; Nolde, F.; De Luca, G.; Cornelissen, J. J. L. M.; Janssen, R. A. J.;Mullen, K.; Rowan, A. E.; Nolte, R. J. M., "The Relationship between Nanoscale Architecture and Function in Photovoltaic Multichromophoric Arrays as Visualized by Kelvin Probe Force Microscopy", *Journal of American Chemical Society* **2008**, *130*, 14605.

25. Zhang, F.; Jonforsen, M.; Johansson, D. M.; Andersson, M. R.; Inganas, O., "Photodiodes and solar cells based on the n-type polymer poly(pyridopyrazine vinylene) as electron acceptor", *Synthetic Metals* **2003**, *138*, 555.

26. Huo, L.; Tan, Z.; Zhou, Y.; Zhou, E.; Han, M.; Li, Y., "Poly(quinoxaline vinylene) With Conjugated Phenylenevinylene Side Chain: A Potential Polymer Acceptor With Broad Absorption Band", *Macromolecular Chemistry and Physics* **2007**, *208*, 1294.

27. Jenekhe, S. A.; Yi, S., "Efficient photovoltaic cells from semiconducting polymer heterojunctions", *Applied Physics Letters* **2000**, *77*, 2635.

28. Alam, M. M.; Jenekhe, S. A., “Efficient Solar Cells from Layered Nanostructures of Donor and Acceptor Conjugated Polymers”, *Chemistry of Materials* **2004**, *16*, 4647.

29. McNeill, C. R.; Abrusci, A.; Zaumseil, J.;Wilson, R.; McKiernan, M. J.; Burroughes, J. H.; Halls, J. J. M.; Greenham, N. C.; Friend, R. H., “Dual electron donor/electron acceptor character of a conjugated polymer in efficient photovoltaic diodes”, *Applied Physics Letters* **2007**, *90*, 193506.

30. Wong, H. M. P.; Wang, P.; Abrusci, A.; Svensson, M.; Andersson, M. R.; Greenham, N. C., “Donor and Acceptor Behavior in a Polyfluorene for Photovoltaics”, *Journal of Physical Chemistry C* **2007**, *111*, 5244.

BIBLOGRAPHY

1. Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C., "Plastic solar cells," *Advanced Functional Materials* **2001**, 11-15.

2. Hoppe, H.; Sariciftci, N. S., "Organic solar cells: An Overview," *Journal of Materials Research* **2004**, *19*, 1924-1945.

3. Nogueira, A. F.; Longo, C.; De Paoli, M. A.," Polymers in dye sensitized solar cells: overview and perspectives," *Coordination Chemistry Reviews* **2004**, *248*, 1455-1468.

4. Spanggaard, H.; Krebs, F. C., "A brief history of the development of organic and polymeric photovoltaics," *Solar Energy Materials and Solar Cells* **2004**, *83*, 125-146.

5. Li, B.; Wang, L. D.; Kang, B. N.; Wang, P.; Qiu, Y., " Review of recent progress in solid state dye sensitized solar cells," *Solar Energy Materials and Solar Cells* **2006**, *90*, 549-573.

6. Riede, M.; Mueller, T.; Tress,W.; Schueppel, R.; Leo, K., " Small molecule solar cells - status and perspectives," *Nanotechnology* **2008**, *19*, 424001.

7. Yum, J. H.; Chen, P.; Gratzel, M.; Nazeeruddin, M. K., "Recent developments in solid-state dye sensitized solar cells," *ChemSusChem* **2008**, *1*, 699–707.

8. Bredas, J. L.; Norton, J. E.; Cornil, J.; Coropceanu, V., "Molecular understanding of organic solar cells: The challenges," *Accounts of Chemical Research* **2009**, *42*, 1691–1699.

9. Wohrle, D.; Meissner, D., "Organic solar cells," *Advanced Materials* **1991**, *3*, 129-138.

10. Nunzi, J. M., "Organic Photovoltaic Materials and Devices," *Comptes Rendus Physique* **2002**, *3*, 523-542.

11. Gregg, B. A., "Excitonic solar cells," *Journal of Physical Chemistry B* 2003,*107*, 4688-4698.

12. Tang, C. W., "Two-layer organic photovoltaic cell," *Applied Physics Letters* **1986**, *48*, 183.

13. Halls, J. J. M.; Pichler, K.; Friend, R. H.; Moratti, S. C.; Holmes, A. B., "Exciton diffusion and dissociation in a poly(*p*-phenylenevinylene)/C-60 heterojunction photovoltaic cell," *Applied Physics Letters* **1996**, *68*, 3120.

14. Haugeneder, A.; Neges, M.; Kallinger, C.; Spirkl, W.; Lemmer, U.; Feldmann, J.; Scherf, U.; Harth, E.; Gugel, A.; Mullen, K., " Exciton diffusion and dissociation in conjugated polymer/fullrene blends and heterostructures," *Physical Review B* **1999**, *59*, 15346-15351.

15. Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J., "Polymer photovoltaic cells: Enhanced efficiencies via a network of internal donor-acceptor heterojunctions," *Science* **1995**, *270*, 1789-1791.

16. Ma, W.; Yang, C.; Gong, X.; Heeger, A. J., "Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating control of morphology," *Advanced Functional Materials* **2005**, *15*, 1617-1622.

17. Ogawa, K.; Stafford, J. A.; Rothstein, S. D.; Tallman, D. E.; Rasmussen, S. C.," Nitrogen- functionalized polythiophenes: Potential routes to new low band gap materials," *Synthetic Metals* **2005,** *152*, 137-140.

18. Shi, C. J.; Yao, Y.; Yang, Y.; Pei, Q. B., "Regioregular copolymers of 3-alkoxythiophene and their photovoltaic application," *Journal of the American Chemical Society* **2006,** *128*, 8980-8986.

19. Murphy, A. R.; Liu, J. S.; Luscombe, C.; Kavulak, D.; Frechet, J. M. J.; Kline, R. J.; McGehee, M. D., "Synthesis, characterization, and field effect transistor performance of carboxylate functionalized polythiophenes with increased air stability," *Chemistry of Materials* **2005,** *17*, 4892-4899.

20. Yurt, S.; Venkatraman B.; Gavallaplli, N.; Venkataraman, D., "Role of molecular architecture in organic photovoltaic cells," *Journal of Physical Chemistry Letters* **2010**, *1*, 947-958.

21. Gavvalapalli, N.; Yurt, S.; Jadhav, K. G.; Venkataraman, D., "Impact of pendant 1, 2, 3-triazole on synthesis and properties of thiophene based polymers," *Macromolecules* **2010**, *43*, 8045-8050.

22. Park, J. W.; Lee, D. H.; Chung, D. S.; Kang, D. M.; Kim, Y. H.; Park, C. E.; Kwon, S. K., "Conformationally Twisted Semiconducting Polythiophene

Derivatives with Alkylthiophene Side Chain: High Solubility and Air Stability", *Macromolecules* **2010**, *43*, 2118–2123.

23. Yu, C. Y.; Ko, B. T.; Ting, C.; Chen, C. P., "Two-dimensional regioregular polythiophenes with conjugated side chains for use in organic solar cells", *Solar Energy Materials and Solar Cells* **2009**, *93*, 613–620.
24. Zou, Y. P.; Sang, G. Y.; Wu, W.P.; Liu, Y. Q.; Li, Y. F., "A polythiophene derivative with octyloxyl triphenylamine-vinylene conjugated side chain: Synthesis and its applications in field-effect transistor and polymer solar cell", *Synthetic Metals* **2009**, *159*, 182–187.
25. He, Y. J.; Wu, W. P.; Liu, Y. Q.; Li, Y. F., "High performance polymer field-effect transistors based on polythiophene derivative with conjugated side chain", *Journal of Polymer Science Part A-1: Polymer Chemistry* **2009**, *47*, 5304–5312.
26. Huang, F.; Chen, K. S.; Yip, H. L.; Hau, S. K.; Acton, O.; Zhang, Y.;Luo, J.D.; Jen, A. K. Y., **"**Development of New Conjugated Polymers with Donor−π-Bridge−Acceptor Side Chains for High Performance Solar Cells", *Journal of American Chemical Society* **2009**, *131*, 13886–13887.
27. Huo, L. J.; Tan, Z. A.; Wang, X.; Zhou, Y.; Han, M. F.; Li, Y. F., "Novel two-dimensional donor–acceptor conjugated polymers containing quinoxaline units: Synthesis, characterization, and photovoltaic properties", *Journal of Polymer Science Part A-1: Polymer Chemistry* **2008**, *46*, 4038–4049.
28. Shen, P.; Sang, G. Y.; Lu, J. J.; Zhao, B.; Wan, M. X.; Zou, Y. P.; Li, Y. F.; Tan, S. T., "Effect of 3D π−π Stacking on Photovoltaic and Electroluminescent

Properties in Triphenylamine-containing Poly(*p*-phenylenevinylene) Derivatives", *Macromolecules* **2008**, *41*, 5716–5722.

29. Price, S. C.; Stuart, A. C.; You, W., "Polycyclic Aromatics with Flanking Thiophenes: Tuning Energy Level and Band Gap of Conjugated Polymers for Bulk Heterojunction Photovoltaics", *Macromolecules* **2010,** *43*, 797-804.
30. Huo, L. J.; Yi, Z.; Li, Y. F., "Alkylthio-Substituted Polythiophene: Absorption and Photovoltaic Properties", *Macromolecular Rapid Communications* **2009,** *30*, 925-931.
31. Ogawa, K.; Stafford, J. A.; Rothstein, S. D.; Tallman, D. E.; Rasmussen, S. C., "Nitrogen-functionalized polythiophenes: Potential routes to new low band gap materials", *Synthetic Metals* **2005,** *152*, 137-140.
32. Shi, C. J.; Yao, Y.; Yang, Y.; Pei, Q. B., "Regioregular Copolymers of 3-Alkoxythiophene and Their Photovoltaic Application", *Journal of American Chemical Society* **2006,** *128*, 8980-8986.
33. Pomerantz, M.; Cheng, Y.; Kasim, R. K.; Elsenbaumer, R. L., "Poly(alkyl thiophene-3-carboxylates).Synthesis, properties and electroluminescence studies of polythiophenes containing a carbonyl group directly attached to the ring", Journal *of Materials Chemistry* **1999,** *9*, 2155-2163.
34. Devasagayaraj, A.; Tour, J. M., "Synthesis of a Conjugated Donor/Acceptor/Passivator (DAP) Polymer", *Macromolecules* **1999,** *32*, 6425-6430.
35. Murphy, A. R.; Liu, J. S.; Luscombe, C.; Kavulak, D.; Frechet, J. M. J.; Kline, R. J.; McGehee, M. D., "Synthesis, Characterization, and Field-Effect Transistor

Performance of Carboxylate-Functionalized Polythiophenes with Increased Air Stability", *Chemistry of Materials* **2005,** *17*, 4892-4899.

36. Yasuda, T.; Imase, T.; Sasaki, S.; Yamamoto, T., "Synthesis, Solid Structure, and Optical Properties of New Thiophene-Based Alternating π-Conjugated Copolymers Containing 4-Alkyl-1,2,4-triazole or 1,3,4-Thiadiazole Unit as the Partner", *Macromolecules* **2005,** *38*, 1500-1503.
37. Ng, S. C.; Ding, M.; Chan, H. S. O.; Yu, W. L., "The Synthesis and Characterization of Fluorescent Poly(heteroaromatic oxadiazole)s", *Macromolecular Chemistry and Physics* **2001,** *202*, 8-13.
38. Yasuda, T.; Namekawa, K.; Iijima, T.; Yamamoto, T., "New luminescent 1,2,4-triazole/thiophene alternating copolymers: Synthesis, characterization, and optical properties", *Polymer* **2007,** *48*, 4375-4384.
39. Kolb, H. C.; Finn, M. G.; Sharpless, K. B., "Click Chemistry: Diverse Chemical Function from a Few Good Reactions", *Angewandte Chemie International Edition* **2001**, *40*, 2004–2021.
40. Fournier, D.; Du Prez, F., ""Click" Chemistry as a Promising Tool for Side-Chain Functionalization of polyurethanes", *Macromolecules* **2008**, *41*, 4622–4630.
41. Binder, W. H.; Sachsenhofer, R., "'Click' Chemistry in Polymer and Materials Science", *Macromolecular Rapid Communications* **2007**, *28*, 15–54.
42. Benanti, T. L.; Kalaydjian, A.; Venkataraman,D., "Protocols for Efficient Postpolymerization Functionalization of Regioregular Polythiophenes", *Macromolecules* **2008**, *41*, 8312–8315.

43. Zeng, Q.; Li, Z.; Li, Z.; Ye, C.; Qin, J.; Tang, B. Z., "Convenient Attachment of Highly Polar Azo Chromophore Moieties to Disubstituted Polyacetylene through Polymer Reactions by Using "Click" Chemistry", *Macromolecules* **2007**, *40*, 5634–5637.

44. Klapars, A.; Buchwald, S. L., "Copper-Catalyzed Halogen Exchange in Aryl Halides: An Aromatic Finkelstein Reaction", *Journal of American Chemical Society* **2002**, *124*, 14844–14845.

45. Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D., "A Simple Method to Prepare Head-to-Tail Coupled, Regioregular Poly(3-alkylthiophenes) Using Grignard Metathesis", *Advanced Materials* **1999**, *11*, 250–253.

46. Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D., "Experimental Evidence for the Quasi-"Living" Nature of the Grignard Metathesis Method for the Synthesis of Regioregular Poly(3-alkylthiophenes)", *Macromolecules* **2005**, *38*, 8649–8656.

47. Boyd, S. D.; Jen, A. K. Y.; Luscombe, C.K., "Steric Stabilization Effects in Nickel-Catalyzed Regioregular Poly(3-hexylthiophene) Synthesis", *Macromolecules* **2009**, *42*, 9387–9389.

48. 27. Loewe, R. S.; Ewbank, P. C.; Liu, J. S.; Zhai, L.; McCullough, R. D., "Regioregular, Head-to-Tail Coupled Poly(3-alkylthiophenes) Made Easy by the GRIM Method: Investigation of the Reaction and the Origin of Regioselectivity", *Macromolecules* **2001**, *34*, 4324–4333.

49. Nagarjuna, G.; Yurt, S.; Jadhav, K.G.; Venkataraman, D., "Impact of Pendant 1,2,3-Triazole on the Synthesis and Properties of Thiophene-Based Polymers", *Macromolecules* **2010**, *43*, 8045– 8050.

50. Zhou, Z.; Fahrni, C. J., "A Fluorogenic Probe for the Copper(I)-Catalyzed Azide−Alkyne Ligation Reaction: Modulation of the Fluorescence Emission via $^3(n,\pi^*)-(\pi,\pi^*)$ Inversion", *Journal of American Chemical Society* **2004**, *126*, 8862–8863.

51. Parent, M.; Mongin, O.; Kamada, K.; Katan, C.; Blanchard- Desce, M., "New chromophores from click chemistry for two-photon absorption and tuneable photoluminescence", *Chemical Communications* **2005**, 2029–2031.

52. Bundgaard, E.; Krebs, F. C., "Low band gap polymers for organic photovoltaics", *Solar Energy Materials and Solar Cells* **2007**, *91*, 954–985.

53. Ajayaghosh, A., "Donor–acceptor type low band gap polymers: polysquaraines and related systems", *Chemical Society Reviews* **2003**, *32*, 181–191.

54. Zeng, G.; Chua, S. J.; Huang, W., "Influence of donor and acceptor substituents on the electronic characteristics of poly(fluorene–phenylene)", *Thin Solid Films* **2002**, *417*, 194–197.

55. Bredas, J. L.; Heeger, A. J., "Influence of donor and acceptor substituents on the electronic characteristics of poly(paraphenylene vinylene) and poly(paraphenylene)", *Chemical Physics Letters* **1994**, *217*, 507–512.

56. Brabec, C. J.; Durrant, J. R., "Solution processed organic solar cells", *MRS Bulletin* **2008**, *33*, 670.

57. Janssen, R. A. J.; Hummelen, J. C.; Saricifici, N. S., "Polymer- fullrene bulk heterojunction solar cells", *MRS Bulletin* **2005**, *30*, 33.

58. Thompson, B. C.; Frechet, J. M. J., "Polymer- fullrene composite solar cells", *Angewandte Chemie International Edition* **2008**, *47*, 58.

59. Dennler, G.; Scharber, M. C.; Brabec, C. J., "Polymer-fullrene bulk heterojunction solar cells" *Advanced Materials* **2009**, *21*, 1323.

60. Boudreault, P. L. T.; Najari, A.; Leclerc, M., "Processable low band gap polymers for photovoltaic applications", *Chemistry of Materials* **2011**, *23*, 456–469.

61. Liang, Y.; Yu, L., "New Class of Semiconducting Polymers for Bulk Heterojunction Solar Cells with Exceptionally High Performance", *Account of Chemical Research* **2010**, *43*, 1227.

62. Chen, J.; Cao, Y., "Development of Novel Conjugated Donor Polymers for High-Efficiency Bulk-Heterojunction Photovoltaic Devices", *Account of Chemical Research* **2009**, *43*, 1709.

63. Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J., "Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions", *Science* **1995**, *270*, 1789.

64. Wienk, M. M.; Kroon, J. M.; Verhees, W. J. H.; Knol, J.; Hummelen, J. C.; van Hal, P. A.; Janssen, R. A. J., "Efficient Methano[70]fullerene/MDMO-PPV Bulk Heterojunction Photovoltaic Cells", *Angewandte Chemie International Edition* **2003**, *42*, 3371.

65. Mihailetchi, V. D.; van Duren, J. K. J.; Blom, P. W. M.; Hummelen, J. C.; Janssen, R. A. J.; Kroon, J. M.; Rispens, M. T.; Verhees, W. J. H.; Wienk, M. M.,

"Electron Transport in a Methanofullerene", *Advanced Functional Materials* **2003**, *13*, 43.

66. Yang, X.; van Duren, J. K. J.; Rispens, M. T.; Hummelen, J. C.; Janssen, R. A. J.; Michels, M. A. J.; Loos, J., "Crystalline Organization of a Methanofullerene as Used for Plastic Solar-Cell Applications", *Advanced Materials* **2004**, 16, 802.
67. Brunetti, F. G.; Gong, X.; Tong, M.; Heeger, A. J.; Wudl, F., "Strain and Hückel Aromaticity: Driving Forces for a Promising New Generation of Electron Acceptors in Organic Electronics", *Angewandte Chemie International Edition* **2010**, 49, 532.
68. Dittmer, J. J.; Marseglia, E. A.; Friend, R. H., "Electron Trapping in Dye/Polymer Blend Photovoltaic Cells", *Advanced Materials* **2000**, 12, 1270.
69. Schmidt-Mende, L.; Fechtenkotter, A.; M€ullen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D., "Self-Organized Discotic Liquid Crystals for High-Efficiency Organic Photovoltaics", *Science* **2001**, *293*, 1119.
70. McNeill, C. R.; Greenham, N. C., "Conjugated-Polymer Blends for Optoelectronics", *Advanced Materials* **2009**, *21*, 3840.
71. Yu, G.; Heeger, A. J., "Charge separation and photovoltaic conversion in polymer composites with internal donor/acceptor heterojunctions", *Journal of Applied Physics* **1995**, *78*, 4510.
72. Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B., "Efficient photodiodes from interpenetrating polymer networks", *Nature* **1995**, *376*, 498.

73. Veenstra, S. C.; Verhees, W. J. H.; Kroon, J. M.; Koetse, M. M.; Sweelssen, J.; Bastiaansen, J. J. A. M.; Schoo, H. F. M.; Yang, X.; Alexeev, A.; Loos, J.; Schubert, U. S.; Wienk, M. M., "Photovoltaic Properties of a Conjugated Polymer Blend of MDMO–PPV and PCNEPV", *Chemistry of Materials* **2004**, *16*, 2503.

74. Kietzke, T.; Horhold, H.-H.; Neher, D., "Efficient Polymer Solar Cells Based on M3EH–PPV", *Chemistry of Materials* **2005**, *17*, 6532.

75. Neuteboom, E. E.; Meskers, S. C. J.; van Hal, P. A.; van Duren, J. K. J.; Meijer, E. W.; Janssen, R. A. J.; Dupin, H.; Pourtois, G.; Cornil, J.; Lazzaroni, R.; Bredas, J. L.; Beljonne, D., "Alternating Oligo(*p*-phenylene vinylene)–Perylene Bisimide Copolymers: Synthesis, Photophysics, and Photovoltaic Properties of a New Class of Donor–Acceptor Materials", *Journal of American Chemical Society* **2003**, *125*, 8625.

76. Zhan, X.; Tan, Z.; Domercq, B.; An, Z.; Zhang, X.; Barlow, S.; Li, Y.; Zhu, D.; Kippelen, B.; Marder, S. R., "A High-Mobility Electron-Transport Polymer with Broad Absorption and Its Use in Field-Effect Transistors and All-Polymer Solar Cells", *Journal of American Chemical Society* **2007**, *129*, 7246.

77. Hou, J.;Zhang, S.;Chen,T.L.;Yang,Y., "A new n-type low bandgap conjugated polymer P-co-CDT: synthesis and excellent reversible electrochemical and electrochromic properties", *Chemical Communications* **2008**, 6034.

78. Huo, L.; Zhou, Y.; Li, Y., "Synthesis and Absorption Spectra of n-Type Conjugated Polymers Based on Perylene Diimide", *Macromolecular Rapid Communications* **2008**, *29*, 1444.

79. Palermo, V.; Otten, M. B. J.; Liscio, A.; Schwartz, E.; de Witte, P. A. J.; Castriciano, M. A.; Wienk, M. M.; Nolde, F.; De Luca, G.; Cornelissen, J. J. L. M.; Janssen, R. A. J.;Mullen, K.; Rowan, A. E.; Nolte, R. J. M., "The Relationship between Nanoscale Architecture and Function in Photovoltaic Multichromophoric Arrays as Visualized by Kelvin Probe Force Microscopy", *Journal of American Chemical Society* **2008**, *130*, 14605.

80. Zhang, F.; Jonforsen, M.; Johansson, D. M.; Andersson, M. R.; Inganas, O., "Photodiodes and solar cells based on the n-type polymer poly(pyridopyrazine vinylene) as electron acceptor", *Synthetic Metals* **2003**, *138*, 555.

81. Huo, L.; Tan, Z.; Zhou, Y.; Zhou, E.; Han, M.; Li, Y., "Poly(quinoxaline vinylene) With Conjugated Phenylenevinylene Side Chain: A Potential Polymer Acceptor With Broad Absorption Band", *Macromolecular Chemistry and Physics* **2007**, *208*, 1294.

82. Jenekhe, S. A.; Yi, S., "Efficient photovoltaic cells from semiconducting polymer heterojunctions", *Applied Physics Letters* **2000**, *77*, 2635.

83. Alam, M. M.; Jenekhe, S. A., "Efficient Solar Cells from Layered Nanostructures of Donor and Acceptor Conjugated Polymers", *Chemistry of Materials* **2004**, *16*, 4647.

84. McNeill, C. R.; Abrusci, A.; Zaumseil, J.;Wilson, R.; McKiernan, M. J.; Burroughes, J. H.; Halls, J. J. M.; Greenham, N. C.; Friend, R. H., "Dual electron donor/electron acceptor character of a conjugated polymer in efficient photovoltaic diodes", *Applied Physics Letters* **2007**, *90*, 193506.

85. Wong, H. M. P.; Wang, P.; Abrusci, A.; Svensson, M.; Andersson, M. R.; Greenham, N. C., "Donor and Acceptor Behavior in a Polyfluorene for Photovoltaics", *Journal of Physical Chemistry C* **2007**, *111*, 5244.